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Citation for published version (APA):

Heuts, J. P. A., Schipper, E. T. W. M., Piet, P., & German, A. L. (1995). Molecular mechanics calculations on cobalt phthalocyanine dimers. *Journal of Molecular Structure: THEOCHEM*, (333), 39-47.
[https://doi.org/10.1016/0166-1280\(94\)03965-N](https://doi.org/10.1016/0166-1280(94)03965-N)

DOI:

[10.1016/0166-1280\(94\)03965-N](https://doi.org/10.1016/0166-1280(94)03965-N)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Journal of Molecular Structure (Theochem) 333 (1995) 39–47

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Molecular mechanics calculations on cobalt phthalocyanine dimers

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Received 15 April 1994; accepted 13 September 1994

Abstract

In order to obtain insight into the structure of cobalt phthalocyanine dimers, molecular mechanics calculations were performed on dimeric cobalt phthalocyanine species. Molecular mechanics calculations are first presented on monomeric cobalt(II) phthalocyanine. Using the Tripos force field for the organic part of the molecule and parameters derived from the literature and subsequently optimized to describe the Co^{II} force field resulted in a geometry that is in very good agreement with experimental data from the literature. Optimization of the dimeric structure leads to a geometry in which both phthalocyanines are separated by 3.2 Å and one of the molecules is shifted 2.38 Å in both the *X*- and *Y*- directions with respect to the other. This geometry is in excellent agreement with literature data on β-Co(pc) crystals and with other calculated and experimental data on similar systems. All calculations were performed with three possible charge distributions in the phthalocyanine molecule and it was shown that varying the charge distribution had no significant effect on the final dimeric structure. This method provides valuable insight into the most important energetic interactions leading to dimer formation.

1. Introduction

In our group we are interested in the effects polymers exhibit on catalytic reactions. Polycations appear to have large promoting effects on the catalytic autoxidation of thiols to disulphides [1–5]. Addition of 2,4-ionene, a poly(quaternary ammonium) salt, to a solution containing the cobalt(II) phthalocyanine-tetrasodiumsulphonate catalyst results in a 40-fold rate enhancement in the mercaptoethanol oxidation as compared with the polymer-free system [2]. Visible light spectroscopy indicates that in the presence of 2,4-ionene

dimerization of the phthalocyanine species occurs, which is assumed to play a major role in the observed rate enhancement [3–6]. These dimeric phthalocyanine species, which are electrostatically stabilized by the polycations, appear to be more active than the monomeric species. In order to get an insight into the interaction between 2,4-ionene and the dimeric cobalt phthalocyanine (Co(pc)) species, we studied the structure of a dimeric Co(pc) species, before modelling the interaction of this species with 2,4-ionene.

A good method for the investigation of the geometries of a great variety of molecules is molecular mechanics (MM), provided that a proper force field, describing the interactions within the molecule, is used. This method has been applied successfully to a wide range of organic molecules for many years

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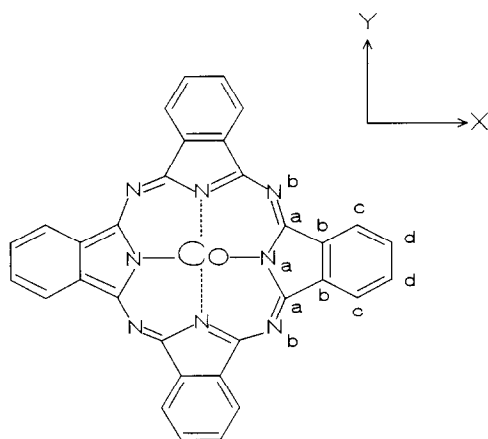


Fig. 1. Labelling scheme of Co(pc) and definition of the coordinate axes.

[7]. In the last decade, there has been a growing interest in the use of MM in inorganic and metallo-organic chemistry [8–17]. A problem with the use of MM for the description of metal–ligand interactions is the absence of force field parameters for most metals, including cobalt, in most commercial MM software packages.

In this study, force field parameters from similar studies [10,12,14–16] were used to estimate the required Co^{II} force field parameters. The modelling of the Co(pc) dimer was performed in two subsequent steps: first we modelled a Co(pc) molecule and then we modelled the interaction between two of these molecules, which is determined merely by electrostatic and Van der Waals interactions [18–22]. Since these interactions are explicitly taken into account in the MM method, MM calculations are very likely to result in rather good geometric predictions for the Co(pc) dimer.

2. Method of calculation

All calculations were performed with the Molecular Mechanics software package SYBYL [23] on the Convex C120 computer of the CAOS/CAMM Centre of Nijmegen University, The Netherlands. Force field parameters used for the description of the organic part of the molecule were taken from the Tripos force field [24] and the following atom

types were used: C.ar for all carbon atoms, N.ar for N_b and N.pl3 for N_a (see Fig. 1). Parameters for the description of the Co^{II} force field were estimated from the literature as described in the following sections and are listed in Table 1. All extra parameters for bonds and angles arising in the dimeric structure were set to zero.

3. Results and discussion

3.1. Modelling of cobalt(II) phthalocyanine

The modelling of Co(pc) consisted of two parts, namely finding good force field parameters for the description of the organic part of the molecule and estimating good parameters for the Co–ligand interactions. Force field parameters for the organic part of the molecule were taken from the Tripos force field [24] without modifications. The chosen atom types (C.ar for all carbon atoms, N.ar for N_b and N.pl3 for N_a) (Fig. 1) yielded overall the best geometry as compared with experimental data [25]

In order to investigate the effect of charge distribution on the final geometry of both the monomer and dimer, we did calculations with three possible charge distributions. As a lower bound for the charge on Co, +1.48e was chosen [25] and as an upper bound, +2e. The most likely charge on Co seems to be +1.88e [26,27], so the results of the calculations for these three cases should cover

Table 1
Force field for Co^{II} in Co(pc)

<i>Bond stretching</i>		
Bond	$r^0/\text{\AA}$	$k/(\text{kcal mol}^{-1} \text{\AA}^{-2})$
Co– N_a	1.92	250
<i>Angle bending</i>		
Angle	θ^0/degree	$k/(\text{kcal mol}^{-1} \text{deg}^{-2})$
Co– N_a – C_a	126.50	1
N_a –Co– N_a	90	0.0013
<i>Van der Waals</i>		
Atom	$r^0/\text{\AA}$	$\epsilon/(\text{kcal mol}^{-1})$
Co	2.35	0.25
<i>Out-of-plane bending</i>		
Atom		$k/(\text{kcal mol}^{-1} \text{\AA}^{-2})$
Co		200

Table 2
Charge distributions for Co(pc) (e)

Atom	Co ^{1.48+} (pc) ^{1.48-} Figgis et al. [25,27]	Co ^{1.88+} (pc) ^{1.88-} Figgis et al. [26,27]	Co ²⁺ (pc) ²⁻ Calculated
Co	+1.48	+1.880	+2.000
N _a	-0.39	-0.337	-0.167
C _a	+0.36	+0.261	+0.095
N _b	-0.42	-0.497	-0.348
C _b	-0.05	-0.065	-0.027
C _c	-0.25 ^a	-0.266	-0.080
C _d	-0.24 ^a	-0.239	-0.083
H _c	+0.16 ^a	+0.239	+0.053
H _d	+0.24 ^a	+0.252	+0.049

^a Estimated from: (C_c + H_c) = -0.09 and (C_d + H_d) = 0.0, and charges of Co^{1.88+} case [25–27].

nearly all possibilities. In the case of Co^{1.48+} and Co^{1.88+}, the corresponding charge distributions in the phthalocyanine ligands were used according to the results of Figgis and coworkers [25–27] (see Table 2), who determined the charge distributions from X-ray experiments. The charge distribution in Co²⁺(pc)²⁻ was calculated by means of the Gasteiger–Hückel [28,29] option within the SYBYL [23] software package. In these calculations we assigned a charge of +2e to Co and the net charge of -2e was distributed within the phthalocyanine ligand. The overall trend of the charge distribution in all three cases is similar.

A first approximation of the equilibrium Co–N_a bond length was determined by the method described by Drew et al. [11]. We first assigned a very high value of 7000 kcal mol⁻¹ Å⁻² to the Co–N stretching force constant and varied the equilibrium Co–N bond length from 1.80 Å to 2.05 Å. Due to the very high stretching force constant of the Co–N bond, the phthalocyanine ligand will adapt its conformation to suit the fixed Co–N bond length. The bond length at which the strain energy of the Co(pc) molecule shows a minimum is a good estimate for the equilibrium Co–N bond length. In Fig. 2 these results are presented for the Co²⁺ case and a deep well is shown at a distance of 1.95 Å. In order to investigate whether this strain energy vs. Co–N distance relation still holds for more realistic stretching force constants, we performed the same calculations with a stretching force constant of 200 kcal mol⁻¹ Å⁻² [13–16,30]. As

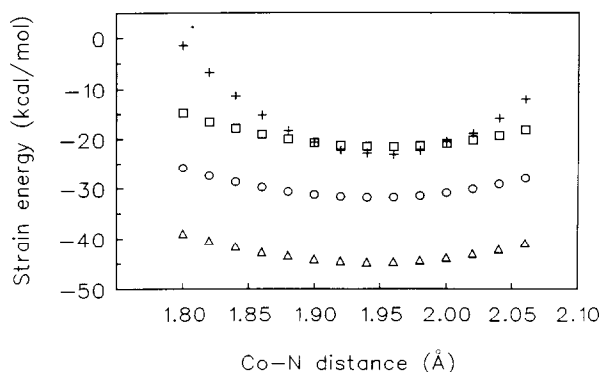


Fig. 2. Plot of steric strain energy (kcal mol⁻¹) against Co–N_a distance (Å) for a Co(pc) monomer: (+), Co²⁺(pc)²⁻, Co–N_a stretching force constant = 7,000 kcal mol⁻¹ Å⁻²; (□), Co²⁺(pc)²⁻, Co–N_a stretching force constant = 200 kcal mol⁻¹ Å⁻²; (Δ), Co^{1.88+}(pc)^{1.88-}, Co–N_a stretching force constant = 200 kcal mol⁻¹ Å⁻²; (○), Co^{1.48+}(pc)^{1.48-}, Co–N_a stretching force constant = 200 kcal mol⁻¹ Å⁻².

can be seen from Fig. 2, again a minimum occurs at 1.95 Å, although the well is shallower than in the case of the very high force constant. A similar pattern was found in the cases of Co^{1.88+} and Co^{1.48+} and the results for the stretching force constant of 200 kcal mol⁻¹ Å⁻² are also depicted in Fig. 2. It can be seen that in all cases a minimum in the strain energy occurs at a distance of 1.95 Å. Furthermore, it can be seen that the curvature in the region of the minimum is small and that the strain energy at a bond length of 1.92 Å is less than 0.3 kcal mol⁻¹ higher than the minimum. Further optimization of the equilibrium bond length was carried out with a starting bond length of 1.95 Å.

Initial estimates for the Co^{II} force field parameters were taken from literature data on similar molecules [12–16,31]. Since many of these data are MM2 values, they seem to be good first estimates for use in the Tripos force field, which is very similar to the MM2 force field.

The Co–N_a bond stretching force constant, equilibrium bond length and Co–N_a–C_a angle bending force constant were varied simultaneously and the optimal combination was found to be: a stretching force constant of 250 kcal mol⁻¹ Å⁻², an equilibrium bond length of 1.92 Å, and an angle bending force constant of 1 kcal mol⁻¹ deg⁻². With these parameters, the calculated Co–N_a

Table 3
Comparison of calculated and experimental bond lengths (Å)

Bond	Calculated Co ^{1.48+} (pc) ^{1.48-}	Calculated Co ^{1.88+} (pc) ^{1.88-}	Calculated Co ²⁺ (pc) ²⁻	Experimental Figgis et al. [25]
Co–N _a	1.935	1.938	1.941	1.919
N _a –C _a	1.346	1.345	1.349	1.380
N _b –C _a	1.337	1.337	1.338	1.325
C _a –C _b	1.394	1.394	1.393	1.457
C _b –C _b	1.386	1.386	1.387	1.398
C _b –C _c	1.395	1.395	1.396	1.397
C _c –C _d	1.401	1.402	1.401	1.396
C _d –C _d	1.404	1.404	1.404	1.410
C _c –H _c	1.086	1.086	1.085	0.96
C _d –H _d	1.087	1.088	1.086	0.98

distance was found to be 1.938 Å for the Co^{1.88+} case, which could be improved to 1.931 Å if the angle bending force constant was lowered to 0.01 kcal mol⁻¹ deg⁻², but then the overall geometry was worse compared to the case of an angle bending force constant of 1 kcal mol⁻¹ deg⁻².

Torsional parameters for torsion angles containing Co were assigned by SYBYL [23] using default values. No attention was paid to these parameters because of their minor importance due to the very rigid structure of Co(pc). Van der Waals parameters for Co(pc) were estimated from the parameters used in low-spin Ni^{II} and Co^{II} studies. The Van der Waals radius for Co^{II} was chosen to be 2.35 Å, which seems to be a good estimate [14]. In contrast to the high ϵ value of 1.65 kcal mol⁻¹ reported in the same paper, we used a value of 0.25 kcal mol⁻¹, which seemed to be more reasonable when compared with other reported ϵ values [12,15,24,32].

The Co^{II} out-of-plane-bending parameter was shown to have a minor effect on the overall energy. This was concluded from the optimization results obtained by energy minimizations using values for the out-of-plane bending force constant of 200 and 10,000 kcal mol⁻¹ Å⁻². In all further calculations a value of 200 kcal mol⁻¹ Å⁻² was used. This seemed to be a good estimate, because Adam et al. [15] used a value of 158 kcal mol⁻¹ Å⁻², in Ni^{II} tetraaza macrocycles, so no further optimizations for this constant were carried out. A summary of the Co^{II} force field parameters used is given in Table 1.

Optimization of the Co(pc) molecule with the

parameters of Table 1 yields geometries that are in excellent agreement with the geometry published by Figgis et al. [25]. The RMS difference in bond lengths for all three investigated charge distribution cases was found to be 0.062 Å if the C–H bond lengths are included and 0.029 Å if they are excluded. The calculated C–H bond lengths in Table 3 converge to the equilibrium C–H bond lengths assigned by SYBYL [23] and are of minor importance for the overall geometry, so it was not necessary to consider them explicitly. Also, a good agreement was found for the bond angles, where the RMS differences were found to be 0.60°, 0.49° and 0.61° for the Co^{1.48+}, Co^{1.88+} and Co²⁺ cases respectively (if the C–C–H angles were excluded, otherwise the RMS values were 0.72°, 0.58° and 0.57°, respectively). The calculated bond lengths and bond angles are compared with the experimental values in Tables 3 and 4.

3.2. Modelling of cobalt(II) phthalocyanine dimer

Modelling of the Co(pc) dimer was carried out by finding the mutual position of two phthalocyanine molecules for which the dimeric strain energy displays a minimum. In order to find this minimum we connected both molecules by a dummy bond and varied the bond length and the torsion angle around this bond. This was done for several different connections, of which the following cases will be discussed here; namely, Co_{Co(pc)1}–Co_{Co(pc)2}, Co_{Co(pc)1}–N_{a,Co(pc)2} and Co_{Co(pc)1}–N_{b,Co(pc)2}. Calculations where Co was attached to the carbon

Table 4
Comparison of calculated and experimental bond angles (°)

Angle	Calculated Co ^{1.48+} (pc) ^{1.48-}	Calculated Co ^{1.88+} (pc) ^{1.88-}	Calculated Co ²⁺ (pc) ²⁻	Experimental Figgis et al. [25]
N _a -Co-N _a	90.0	90.0	90.0	90.0
Co-N _a -C _a	126.60	126.60	126.59	126.50
C _a -N _b -C _a	122.46	122.86	122.90	121.07
C _a -N _a -C _a	106.79	106.78	106.81	107.00
N _b -C _a -N _a	127.09	126.97	126.88	127.93
N _b -C _a -C _b	122.44	122.65	122.74	121.93
N _a -C _a -C _b	110.44	110.49	110.38	110.14
C _a -C _b -C _c	132.44	132.40	132.22	132.06
C _a -C _b -C _b	106.14	106.15	106.23	106.36
C _b -C _b -C _c	121.45	121.44	121.43	121.58
C _b -C _c -C _d	117.50	117.58	117.45	117.06
C _c -C _d -C _d	121.03	120.94	121.02	121.36
C _b -C _c -H _c	120.48	119.81	120.95	121.2
C _d -C _c -H _c	122.04	122.54	121.54	121.7
C _c -C _d -H _d	119.21	119.41	119.44	119.9
C _d -C _d -H _d	119.86	119.67	119.54	118.8

atoms were also performed, but these all lead to higher energies than the Co–N linked dimers.

All new force constants occurring due to the several new bonds and angles formed in the “super molecule” were set to zero, so no additional parameters have been added. This enables us to compare the energies of the several conformations objectively. Calculations on these dimeric structures have been performed for cobalt phthalocyanines with the three charge distributions mentioned. For clarity, only the results for

Co^{1.88-}(pc)^{1.88-} will be shown in the figures and the differences with the other two cases will be discussed.

3.2.1. Case I: dimers through Co–Co linkage

For Co^{1.88+}(pc)^{1.88-}, a minimum of $-94.5 \text{ kcal mol}^{-1}$ was found in the overall dimeric strain energy upon decreasing the defined Co–Co bond from 6 to 2 Å, as can be seen in Fig. 3. However, the actual interplanar separation does not correspond to the defined Co–Co distance. As can be seen from Fig. 4a and 4b, the Co–Co distance converges to about 4.1 Å whereas the interligand distance converges to about 3.3 Å upon decreasing the defined Co–Co bond length. Optimizations of starting conformations in which the connecting bond length is smaller than about 3.6 Å lead to almost the same energy and geometry irrespective of the starting conformation. Only very small defined separations ($\approx 1.5 \text{ Å}$) do not lead to a realistic optimized structure. For the two other charge distribution cases a similar pattern was found. The final interligand distance for the latter two cases is the same as in the Co^{1.88+}(pc)^{1.88-} case. The fact that the Co–Co distance does not converge to the same value as the interligand distance is due to the strong electrostatic repulsion between the two relatively high charges on the Co centres

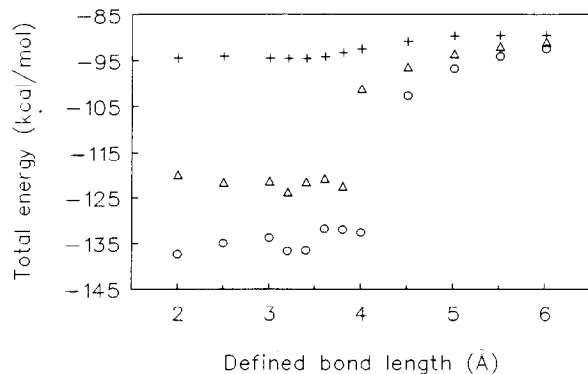


Fig. 3. Total energy (kcal mol^{-1}) as a function of the defined connecting bond length (Å) in a Co^{1.88+}(pc)^{1.88-} dimer: (+), case I: Co–Co linkage; (Δ), case II: Co–N_a linkage; (○), case III: Co–N_b linkage.

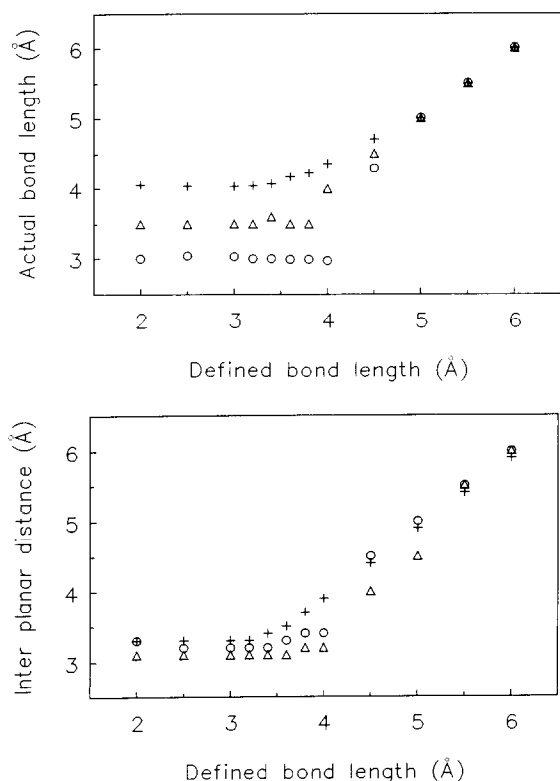


Fig. 4. (a) Plot of the length of the connecting bond (Å) in the $\text{Co}^{1.88+}(\text{pc})^{1.88-}$ dimer after optimization against the defined connecting bond length (Å): (+), case I: Co–Co linkage; (Δ), case II: Co–N_a linkage; (\circ), case III: Co–N_b linkage. (b) Plot of the average interplanar distance (Å) in the $\text{Co}^{1.88+}(\text{pc})^{1.88-}$ dimer after optimization against the defined connecting bond length (Å): (+), case I: Co–Co linkage; (Δ), case II: Co–N_a linkage; (\circ), case III: Co–N_b linkage.

and even a stretching force constant of $10,000 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$ used for the Co–Co bond had no influence on this optimized distance.

The main energetic contributions to the stabilization of the dimer consist of Van der Waals and

electrostatic interactions. If the sum of the energy changes in electrostatic and Van der Waals contributions going from the monomer to the dimer (see Table 5a) is considered, then it can be seen that on average the stabilizing effect is about 3 kcal mol^{-1} larger than the calculated energy of dimerization, here defined as the energy difference between the stable dimer and a pair of phthalocyanine molecules at 6 Å distance. This extra stabilization is compensated by a slight increase in the internal strain of a monomeric phthalocyanine arising from the dimer formation.

From these results it can be concluded that by optimizing the electrostatic and Van der Waals interactions in the dimer, a more favorable dimer conformation can be obtained.

In order to find a better conformation within the Co–Co bond approach, we varied the N_a–Co–Co–N_a torsion angle, but the lowest energy was obtained for the eclipsed face-to-face dimeric conformation. The staggered conformation (rotated by 45° about the Z-axis) has an energy about 3 kcal mol^{-1} higher than the eclipsed conformation.

3.2.2. Case II: dimers through Co–N_a linkage

In the case of linkage between Co and N_a, a minimum of $-123.8 \text{ kcal mol}^{-1}$ was found upon decreasing the defined Co–N_a bond length from 6 Å to 2 Å, which is depicted in Fig. 3. As can be seen from Fig. 4a and b, the interplanar distance in these dimers converges to about 3.1 Å, whereas the Co–N_a distance converges to about 3.5 Å. Rotation of the two molecules with respect to each other via the linkage does not lead to an energetically more favourable conformation. Similar to the case of the Co–Co linked dimers, the most favourable conformation is an eclipsed face-to-face conformation, but now one of the molecules has

Table 5a

Comparison of the results for the dimers of $\text{Co}^{2+}(\text{pc})^{2-}$, $\text{Co}^{1.88+}(\text{pc})^{1.88-}$ and $\text{Co}^{1.48+}(\text{pc})^{1.48-}$. Case I: dimers through Co–Co linkage

	$\text{Co}^{2+}(\text{pc})^{2-}$	$\text{Co}^{1.88+}(\text{pc})^{1.88-}$	$\text{Co}^{1.48+}(\text{pc})^{1.48-}$
Optimized Co–Co length/Å	4.2	4.1	3.9
Interplanar separation/Å	3.3	3.3	3.3
Dimerization energy/(kcal mol^{-1})	-13.3	-5.1	-10.9
Change in Van der Waals energy/(kcal mol^{-1})	-32.8	-32.1	-33.0
Change in electrostatic energy/(kcal mol^{-1})	15.0	24.3	19.9

Table 5b

Comparison of the results for the dimers of $\text{Co}^{2+}(\text{pc})^{2-}$, $\text{Co}^{1.88+}(\text{pc})^{1.88-}$ and $\text{Co}^{1.48+}(\text{pc})^{1.48-}$. Case II: dimers through $\text{Co}-\text{N}_a$ linkage

	$\text{Co}^{2+}(\text{pc})^{2-}$	$\text{Co}^{1.88+}(\text{pc})^{1.88-}$	$\text{Co}^{1.48+}(\text{pc})^{1.48-}$
Optimized $\text{Co}-\text{N}_a$ length/Å	3.5	3.5	3.5
Interplanar separation/Å	3.1	3.1	3.1
Dimerization energy/(kcal mol ⁻¹)	-23.4	-32.8	-25.7
Change in Van der Waals energy/(kcal mol ⁻¹)	-35.2	-32.3	-34.5
Change in electrostatic energy/(kcal mol ⁻¹)	8.5	-0.4	7.2

been moved 1.94 Å in the *X*- (or *Y*-)direction parallel to the other molecule. Compared to the most favourable dimer via $\text{Co}-\text{Co}$ linkage, these dimers are energetically more favourable, as was to be expected, because of a smaller electrostatic repulsion. The behaviour of the other two charge distribution cases is similar and the final geometries are the same as found in the $\text{Co}^{1.88+}(\text{pc})^{1.88-}$ case (see Table 5b).

3.2.3. Case III: dimers through $\text{Co}-\text{N}_b$ linkage

Linkage of the two phthalocyanine molecules via a $\text{Co}-\text{N}_b$ linkage resulted in an energy that was much lower than obtained in both the other two cases. As can be seen from Fig. 3, the minimum energy is $-136.6 \text{ kcal mol}^{-1}$ in the case of $\text{Co}^{1.88+}(\text{pc})^{1.88-}$. This lower energy cannot be explained by a difference in Van der Waals interactions, because these are of comparable magnitude in all three cases and are even higher in this case. The reason for the extra stabilization lies in the fact that the electrostatic repulsion is significantly lower than in the other two cases and even decreases going from 6 Å to 2 Å.

As can be seen from Fig. 4a and b, the final interplanar distance is 3.2 Å and the final $\text{Co}-\text{N}_b$ distance is 3.0 Å. This geometry thus consists of two phthalocyanines at a separation of 3.2 Å and one phthalocyanine moved parallel with respect to the other, 2.38 Å in the *X*- and 2.38 Å in the *Y*-directions. As in cases I and II, we tried to optimize the structure by rotation about the connecting bond, but again the non-rotated conformation was most stable. A representation of the optimal geometry is given in Fig. 5.

3.2.4. Comparison of the three linkage cases

A summary of the most important results obtained

in this study is given in Tables 5a–c. As can be seen from these tables and Fig. 3, the dimers of case III geometry are more stable than both the other two dimers. Since the Van der Waals stabilization is almost the same in all three cases, the main cause of the difference in dimerization energy is the lower electrostatic repulsion in case III. Noting that the Van der Waals interactions have a larger magnitude than the electrostatic interactions, it may be concluded that the Van der Waals interactions are the predominant factor in the stabilization of the dimer, but that the final geometry is determined by the electrostatic interactions, which is in agreement with other studies [33,34].

Furthermore, the most favourable conformation is one that has been translated in only the *X*- and *Y*-directions and not rotated about the *Z*-axis. This is in agreement with the fact that π -stacked

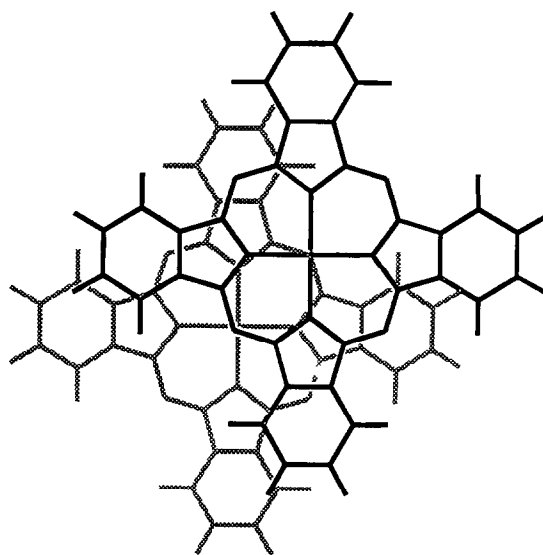
Fig. 5. Optimized geometry of $\text{Co}(\text{pc})$ dimer.

Table 5c

Comparison of the results for the dimers of $\text{Co}^{2+}(\text{pc})^{2-}$, $\text{Co}^{1.88+}(\text{pc})^{1.88-}$ and $\text{Co}^{1.48+}(\text{pc})^{1.48-}$. Case III: dimers through Co–N_b linkage

	$\text{Co}^{2+}(\text{pc})^{2-}$	$\text{Co}^{1.88+}(\text{pc})^{1.88-}$	$\text{Co}^{1.48+}(\text{pc})^{1.48-}$
Optimized Co–N _b length/Å	3.1	3.0	3.2
Interplanar separation/Å	3.1	3.2	3.2
Dimerization energy/(kcal mol ⁻¹)	-38.9	-44.3	-34.3
Change in Van der Waals energy/(kcal mol ⁻¹)	-28.2	-25.7	-32.0
Change in electrostatic energy/(kcal mol ⁻¹)	-11.5	-13.8	-3.5

porphyrins are not found in a rotated conformation [33], but in disagreement with other MM calculations which predicted geometries in which one phthalocyanine or porphine ring was rotated about the *Z*-axis [34]. However, these authors did not present the energy difference between the eclipsed and staggered conformations, so it is not clear if this rotation contributes much to an extra stabilization of the dimer. Anderson et al. [35] performed MO calculations on Si(pc)–O–Si(pc) dimers and found that a dimer, in which the phthalocyanines were rotated 45° with respect to each other, was favoured over an eclipsed conformation by only 1 kcal mol⁻¹. This difference was not enough to conclude that the rotated dimer was more favourable than the eclipsed face-to-face conformation. Also the calculations of Sudhindra and Fuhrhop on porphine dimers [18] showed a very small energy difference (0.7 kcal mol⁻¹) between an eclipsed face-to-face dimer and a dimer in which one molecule was rotated about the *Z*-axis by 60°, which was the optimal geometry.

The parallel shifts in *X*- and *Y*- directions leading to more stable geometries are in good agreement with earlier experimental and calculated data. Hunter and Sanders [33] stated that rotations are not likely to occur, but an optimization of the energy can be achieved by parallel shifts of one molecule in both *X*- and *Y*-directions. They ascribe these shifts to π – π repulsion terms. Similar shifts are observed in phthalocyanine crystals. Our results are in excellent agreement with experimental data published on β -Co(pc) crystals [36,37]. X-ray diffraction results at 295 K indicate a dimeric structure, similar to our structure, in which the Co of one phthalocyanine faces the N_b of another phthalocyanine molecule at a separation of

3.219 Å [36]. Single-crystal neutron diffraction methods at 4.3 K give the same structure in which the Co–N_b distance is now 3.154 Å [37]. Crystallographic studies on other phthalocyanine structures indicate comparable *X*- and *Y*-shifts [38,39].

4. Conclusions

The modelling of a cobalt(II) phthalocyanine molecule was very successful using the Tripos force field and some additional parameters estimated from the literature. Excellent agreement with earlier reported crystallographic data on β -Co(pc) was obtained. Our results are also in agreement with calculated and experimental data on similar systems, which indicates the successful applicability of MM to these systems. Our method for modelling the dimeric structure of Co(pc) resulted in an optimized structure in which one of the molecules was shifted 2.38 Å in both the *X*- and *Y*-directions with respect to the other. The interplanar separation in this geometry is 3.2 Å, which is the same as found in β -Co(pc) crystals.

Furthermore, it was shown that the three charge distributions used yielded qualitatively comparable results, which indicates that the trend in the charge distribution is more important than the absolute values. The results also indicate that the Van der Waals interactions are the predominant factor in stabilizing the dimer, because the Van der Waals interactions have a larger magnitude than the electrostatic interactions, but the electrostatic interactions mainly determine the final geometry. Since our method is very straightforward we believe that it is very useful in modelling the interactions between larger molecules and that this will lead to (at least qualitatively) good results.

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