Structure of 5,5-Dimethyl-2-(4-nitrophenylaminomethylene)-1,3-cyclohexanedione

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Abstract. $C_{15}H_{16}N_2O_4$, triclinic, $P\bar{1}$, $a = 12{\cdot}719\,(3)$, $b = 7{\cdot}485\,(2)$, $c = 7{\cdot}728\,(2)$ Å, $\alpha = 93{\cdot}18\,(2)$, $\beta = 100{\cdot}40\,(2)$, $\gamma = 99{\cdot}24\,(2)°$, $V = 711{\cdot}5\,(3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}35$, $D_x = 1{\cdot}34$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}092$ mm^{-1}, $F(000) = 304$, $T = 300$ K, final $R = 0{\cdot}08$ for 1124 observed reflections. The IR, Raman and ^{1}H NMR spectra of 2,2-diacylethenamines and 2-aminomethylene-5,5-dimethylcyclohexane-1,3-diones show that these substances exist exclusively in the chelated enaminodiketone form and that the conjugated system contained in them is essentially planar [Gómez-Sánchez, García Martin, Borrachero & Bellanato (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 301–306]. The molecule has an intramolecular hydrogen bond between the N(amino) and O(carbonyl) atoms. The packing of the molecules is governed by normal van der Waals contacts.

Introduction. The title compound (1) was synthesized according to the literature and was obtained from 5,5-dimethylcyclohexane-1,3-dione, triethyl ortho-formate and *p*-nitroaniline as described by Wolfbeis & Ziegler (1976).

(1)
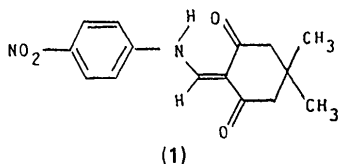
The vibrational spectra of 2,2-diacyclethenamines ('enaminodiones') are interesting because of the information they provide on the electron distribution inside these mesomeric systems and on the conformations they can adopt (Gómez-Sánchez, García Martin, Borrachero & Bellanto, 1987). In order to obtain a better understanding of the relationship between the vibrational specta and conformations of enaminodiones, an X-ray crystallographic study has been carried out.

Experimental. Single crystals of the title compound were in the form of colourless prisms with well shaped faces. The specimen used had approximate dimensions $0{\cdot}16 \times 0{\cdot}35 \times 0{\cdot}18$ mm. D_m was measured by flotation. Unit-cell parameters were obtained from the least-squares refinement of θ values of 25 reflections within the range $4 < \theta < 13°$. A Nonius CAD-4 diffractometer was used with monochromated Mo $K\alpha$ radiation; $\omega/2\theta$ mode, $2\theta_{max} = 42°$ ($-12 \le h \le 12$, $-7 \le k \le 7$, $0 \le l \le 6$). Two reference reflections ($1\bar{2}1$ and $\bar{4}22$) were measured every hour to monitor crystal stability and were re-centred after every hundred measured reflections to monitor crystal orientation. No significant changes in intensities were noted. From 1637 measured reflections, 1124 were observed with $I \ge 2\sigma(I)$. Corrections were made for Lorentz–polarization effects, but not for extinction and absorption. This last effect was not taken into account because the crystal absorption with Mo radiation was practically negligible.

The structure was solved by direct methods using the *MULTAN*80 program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). 334 reflections with $E > 2{\cdot}5$ and four reflections in the starting set were used to determine the structure. The initial E map revealed most of the non-H atoms and the remainder were located from subsequent electron-density maps. After anisotropic refinement by full-matrix least squares of all of the 21 non-H atoms in the asymmetric unit, the H atoms were located at geometrical positions. The H atoms were assigned the same isotropic thermal parameters as the atoms to which they were bonded and were included, but not refined, in the final stage of refinement.

Refinement was based on F (structure amplitudes) to minimize the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$; 190 parameters were refined (nine parameters per non-H atom plus one for the scale); the over-determination ratio was $5{\cdot}9$ reflections/parameter. The refinement led to a final convergence with $R = 0{\cdot}080$, $wR = 0{\cdot}079$. All parameter shifts during the final cycle of refinement were less than $0{\cdot}20\sigma$. Max. and min. heights in the final difference Fourier synthesis were $0{\cdot}3$ and $-0{\cdot}3$ e Å^{-3}. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1962, Vol. III), and all calcu-

Table 1. *Non*-H *atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^3$), *with e.s.d.'s in parentheses*

$$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(a_i,a_j).$$

	x	y	z	U_{eq} (Å²)
N(1)	8660 (7)	3428 (10)	7469 (11)	50 (3)
N(2)	12025 (7)	9090 (11)	6883 (14)	60 (4)
O(13)	6559 (6)	2416 (9)	6814 (13)	83 (4)
O(15)	8759 (6)	−1267 (9)	9925 (12)	75 (4)
O(21)	12931 (6)	9027 (10)	7572 (14)	85 (4)
O(22)	11737 (7)	10348 (10)	6031 (14)	88 (4)
C(1)	5926 (7)	−2315 (11)	7673 (13)	41 (3)
C(2)	5693 (7)	−318 (12)	7720 (17)	60 (4)
C(3)	6697 (8)	1027 (11)	7557 (14)	44 (3)
C(4)	7731 (8)	664 (12)	8292 (13)	43 (3)
C(5)	7905 (9)	−1001 (12)	9178 (13)	48 (4)
C(6)	6858 (8)	−2364 (11)	9138 (13)	49 (4)
C(7)	8685 (8)	1846 (11)	8249 (13)	41 (3)
C(8)	9573 (8)	4774 (11)	7364 (13)	42 (3)
C(9)	9294 (8)	6309 (12)	6578 (14)	49 (4)
C(10)	10081 (9)	7730 (13)	6396 (17)	59 (4)
C(11)	11131 (9)	7584 (12)	7021 (14)	49 (4)
C(12)	11437 (8)	6081 (13)	7833 (15)	50 (4)
C(13)	10613 (8)	4649 (12)	8005 (16)	55 (4)
C(21)	6128 (9)	−2859 (12)	5895 (15)	57 (4)
C(31)	4888 (8)	−3523 (13)	8032 (17)	60 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

|			
N(1)—C(7)	1·361 (11)	N(2)—C(11)	1·490 (13)
N(1)—C(8)	1·426 (11)	C(2)—C(3)	1·522 (12)
O(13)—C(3)	1·236 (12)	C(2)—C(1)	1·569 (13)
O(15)—C(5)	1·186 (13)	C(11)—C(12)	1·393 (14)
C(13)—C(12)	1·403 (13)	C(11)—C(10)	1·359 (15)
C(13)—C(8)	1·346 (14)	C(9)—C(8)	1·394 (13)
C(4)—C(7)	1·388 (12)	C(9)—C(10)	1·370 (13)
C(4)—C(5)	1·483 (13)	C(5)—C(6)	1·535 (13)
C(4)—C(3)	1·410 (13)	C(6)—C(1)	1·491 (13)
N(2)—O(21)	1·189 (12)	C(21)—C(1)	1·489 (15)
N(2)—O(22)	1·243 (13)	C(1)—C(31)	1·553 (13)
C(7)—N(1)—C(8)	126·5 (8)	O(15)—C(5)—C(6)	121·3 (8)
C(12)—C(13)—C(8)	119·0 (8)	C(5)—C(6)—C(1)	117·2 (7)
C(5)—C(4)—C(3)	123·5 (8)	C(13)—C(12)—C(11)	117·8 (9)
C(7)—C(4)—C(3)	122·7 (8)	C(4)—C(3)—C(2)	119·0 (8)
C(7)—C(4)—C(5)	113·7 (8)	O(13)—C(3)—C(2)	117·8 (8)
O(22)—N(2)—C(11)	115·0 (9)	O(13)—C(3)—C(4)	123·1 (8)
O(21)—N(2)—C(11)	119·7 (8)	C(13)—C(8)—C(9)	121·6 (9)
O(21)—N(2)—O(22)	125·2 (9)	N(1)—C(8)—C(9)	113·6 (8)
C(3)—C(2)—C(1)	111·0 (7)	N(1)—C(8)—C(13)	124·6 (8)
N(2)—C(11)—C(10)	120·1 (8)	C(11)—C(10)—C(9)	117·4 (9)
N(2)—C(11)—C(12)	116·4 (9)	C(6)—C(1)—C(21)	113·7 (8)
C(12)—C(11)—C(10)	123·3 (9)	C(2)—C(1)—C(21)	109·3 (8)
N(1)—C(7)—C(4)	120·7 (8)	C(2)—C(1)—C(6)	107·1 (7)
C(8)—C(9)—C(10)	120·6 (9)	C(21)—C(1)—C(31)	110·3 (8)
O(15)—C(5)—C(4)	124·5 (9)	C(6)—C(1)—C(31)	109·8 (8)
C(4)—C(5)—C(6)	114·0 (8)	C(2)—C(1)—C(31)	106·0 (7)

lations were carried out with the *XRAY*70 (Stewart, Kundell & Baldwin, 1970) system. The high *R* value is due to poor crystal quality. Bond lengths and angles were calculated with *PARST* (Nardelli, 1983).

Discussion. The positional and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* Bond lengths and angles are given in Table 2. The C—H distances range from 0·99 to 1·03 Å. A view (*ORTEP*; Johnson, 1976) of the molecule along

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54247 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the *b* axis with the atomic numbering is shown in Fig. 1.

The results clearly indicate the existence of extensive electron delocalization involving the donor N(1) and the two acceptor carbonyl groups C(6)—O(13) and C(5)—O(15). Bond lengths and angles agree well with those reported for analogous compounds (Vickery, Willey & Drew, 1985) and with those containing analogous resonance systems (Diánez, López-Castro & Márquez, 1985, 1987). Angles at C(1) are in the range 106–114°, as expected for an sp^3 C atom. The C(4)—C(7) bond distance [1·388 (12) Å] is significantly longer than a formal C=C bond (1·336 Å) (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965) and there is also a corresponding shortening of the N(1)—C(7) bond [1·361 (11) Å] which is shorter than the 1·452 Å reported (Ammon, Mazzochi, Regan & Colicelli, 1979) for an N—C(sp^2) bond. On the acceptor side, the C(4)—C(5) and C(3)—C(4) bonds are 1·483 (13) and 1·410 (3) Å, which are also shorter than the 1·487 Å value reported (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973) for a C(sp^2)—C(sp^2) single bond. The system

C(5)—O(15)
/
N(1)—C(7)—C(4)
\
C(3)—O(13)
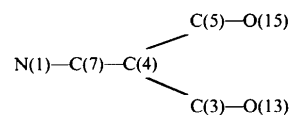
is approximately planar [max. deviation from the best square plane, 0·046 (10) Å], and C(2) and C(6) are nearly in the same plane [max. deviation, 0·087 (10) Å] which agrees well with the half-boat conformation found for the cyclohexane ring and is also consistent with the quasi-planarity of the resonance system. Cremer & Pople (1975) puckering
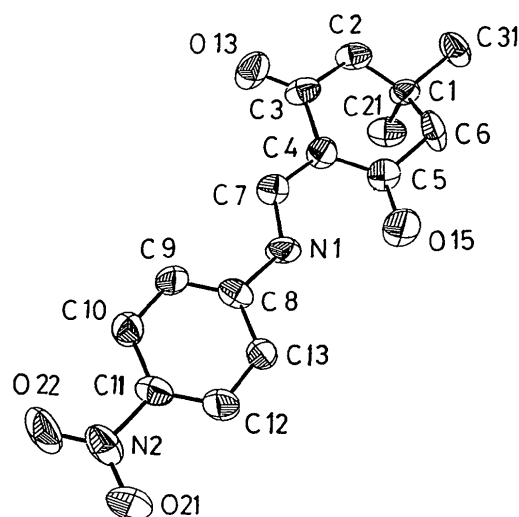

Fig. 1. *ORTEP* (Johnson, 1976) view of the title molecule along the *b* axis showing the atomic numbering scheme. Thermal ellipsoids enclose 50% probability.

parameters for the sequence C(1)—C(2)—C(3)—C(4)—C(5)—C(6) are $Q = 0.50$ Å, $\varphi = -171°$ and $\theta = 125°$ and Nardelli (1983) asymmetry parameters are $\Delta C_s[C(1)] = 0.041$ and $\Delta C_2[C(2)—C(1)] = 0.084$. The torsion angles around the C(4)—C(7) double bond are ~179°.

Additional distortion of the cyclohexanedione ring is also due to the O(13) and O(15) substituents in equatorial positions; this agrees with previous results (de Kok & Romers, 1970; Nader, 1975) which show that substituents at C(3) and C(5) in equatorial positions affect the torsion angles and so the heterocycle conformation.

The *p*-nitrophenyl group is nearly planar [max. deviation to the mean-square plane 0.078 (10) Å]; although there is a slight tilt, 6.1 (7)° around N(2)—C(11), of the nitro group with respect to the phenyl plane of atoms.

The X-ray structure analysis of related compounds (Diánez, López-Castro & Márquez, 1985, 1987) shows that the *ZZE*-enaminodione system is strictly planar and the close similarity between the *IR* spectra for solids and solutions of these compounds and for other compounds examined (Gómez-Sánchez, García Martín, Borrachero & Bellanato, 1987) indicates that the aminomethylene-5,5-dimethylcyclohexane-1,3-dione moiety of all of them has the same conformation.

As expected there is an intramolecular hydrogen bond between the N(1) atom and the carbonyl oxygen O(13). $N(1)\cdots O(13) = 2.606$ (11) Å and $N(1)—H\cdots O(13) = 133$ (1)°, showing a chelated structure. There are no intermolecular distances less than the sum of the van der Waals radii.

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Structure of 3-Methoxypyrazine-2-carbaldehyde 2,4-Dinitrophenylhydrazone

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Abstract. $C_{12}H_{10}N_6O_5$, $M_r = 318.25$, monoclinic, $P2_1/c$, $a = 7.1026$ (9), $b = 9.404$ (2), $c = 21.372$ (2) Å, $\beta = 108.246$ (9)°, $V = 1355.8$ (7) Å³, $Z = 4$, $D_x = 1.559$ g cm⁻³, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 10.26$ cm⁻¹, $F(000) = 656$, $T = 296$ K, $R = 0.087$ for 1083 observed $[I/\sigma(I) \geq 3]$ reflexions. All skeletal atoms in the title phenylhydrazone lie in one plane, including the methoxyl methyl and the nitro-group O atoms, with a mean deviation from the plane of only 0.0455 Å. The imine double bond has Z geometry and the benzenoid ring is oriented so that the *ortho*-nitro group is *syn* to the side-chain NH. The structure of the phenylhydrazone demonstrates that free-radical substitution of 2-methoxypyrazine in acid solution takes place *ortho* to the methoxyl and α to the more basic N atom.

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