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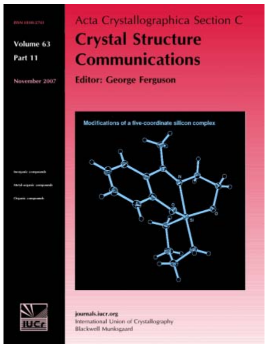

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Interaction between a dimethylamino group and an electron-deficient alkene in ethyl (*E*)-2-cyano-3-(8-dimethylamino-1-naphthyl)propenoate

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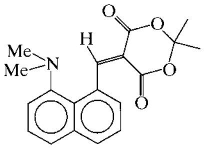
The interaction between the *peri* substituents in the title compound, $C_{18}H_{18}N_2O_2$, measured at 150 K, represents an early stage in the addition reaction of an amino group to an electron-deficient alkene, and has an $N\cdots Csp^2$ separation of 2.531 (2) Å; comparison with related structures indicates that the nitrile group activates an alkene to nucleophilic attack more than a coplanar carboxylic ester group.

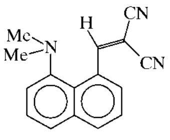
Comment

Studies of interactions between closely placed functional groups have been used to model the progress of the corresponding chemical reactions. Particular success has been obtained for addition of an amino group to a carbonyl bond, for which a variety of compounds model different stages in the reaction (Bürgi *et al.*, 1973; Schweizer *et al.*, 1978). Recently, we extended this approach to examine the Michael reaction between an amino group and an electron-deficient alkene (Bell & Wallis, 1999) using the *peri*-substituted naphthalene derivatives (I)–(III). These compounds showed different degrees of $N\cdots Csp^2$ interaction. Compound (I) has a structure much nearer to the zwitterionic enolate (IV) with an $Me_2N{-}C(CX_2)$ bond length of 1.651 (3) Å while compounds (II) and (III) show $Me_2N\cdots C{=}CX_2$ separations of 2.413 (2) and 2.679 (2) Å, respectively. The theoretical axis of the N atom's lone pair lies at a smaller angle to the $N\cdots C$ interaction vector in (II) (*ca* 13°) than in (III) (*ca* 30°). To extend these studies we have prepared the analogous compound (V) which was isolated as the only product of the Knoevenagel condensation of ethyl cyanoacetate and 8-dimethylaminonaphthalene-1-carbaldehyde. To determine the stereochemistry of this alkene and to compare the interaction between the *peri*-substituents with those in (I)–(III), the structure of (V) has been determined by X-ray diffraction at 150 K.

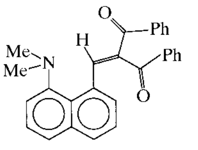
The molecular structure of (V) is shown in Fig. 1 and selected geometric data are given in Tables 1 and 2. The stereochemistry about the double bond puts the less bulky nitrile group *cis* to the naphthalene ring. In contrast to the two carbonyl groups of derivative (III), the carboxy group of (V) lies nearly coplanar with the alkene [O1—C14—C12—C13 5.5 (3), O2—C14—C12—C11 9.4 (3)°]. The best plane of the cyanoethenoate residue (C11, C12, C13, C14, N2, O1, O2) lies at 64.8 (1)° to that of the naphthalene ring. The dimethylamino group is oriented so that the N atom's lone pair is directed towards the other *peri* substituent. The shortest contact between *peri* groups is between the two atoms directly attached to the naphthalene skeleton; the $N1\cdots C11$ separation is 2.531 (2) Å, *ca* 0.7 Å within the sum of the van der Waals radii of C and N atoms. The interaction mimics an early stage in the Michael reaction between an amino group and an electron-deficient alkene. The two substituents are displaced slightly to opposite sides of the best naphthalene plane [N1 by 0.083 (2), C11 by 0.140 (2) Å] and the angle between the $N1\cdots C11$ vector and the alkene bond is 114.36 (12)°. In the plane of the naphthalene ring the dimethylamino group is displaced from its theoretical position by 3.2° towards the



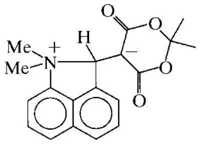
(I)



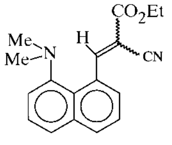
(II)



(III)



(IV)



(V)

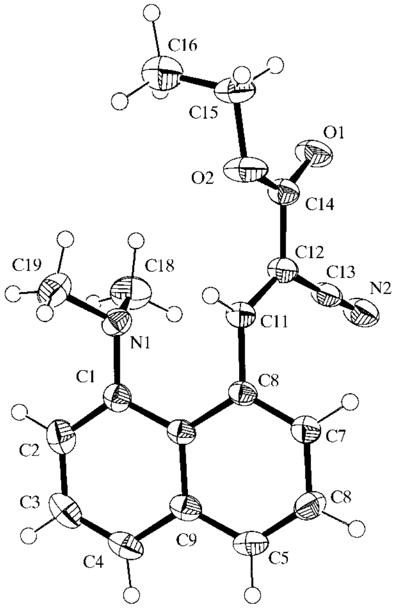


Figure 1
*ORTEP*III (Johnson & Burnett, 1996) drawing of the title compound with anisotropic displacement parameters drawn at the 50% level.

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alkene which is displaced away by 1.5° in the same sense. The theoretical position of the amino N atom's lone pair axis lies at 18° to the N1···C11 vector. There are no significant short intermolecular contacts consistent with the low density of the crystal.

The molecular geometry of compound (V) is intermediate between those of compounds (II) and (III) as illustrated by a variety of geometric parameters (Table 2) including the N1···C11 separation, the alkene bond length and the in-plane displacements of the *peri* functional groups. However in one respect, structure (V) is much closer to that of (II); the axes of the N atoms' lone pairs are both fairly closely aligned with the N1···C11 vector, and consistent with a weak bonding interaction between the functional groups. In contrast the alignment in (III) is much poorer.

The structural measurements on (II) and (V) which differ only in the replacement of a nitrile group with a carboxylic ester afford a comparison of the effects of the electron-withdrawing capacities of these groups on the reactivity of an alkene bond to nucleophiles. The nitrile group appears to be the superior since the interaction between the dimethylamino group and the alkene progresses further along the reaction coordinate for the Michael reaction in dinitrile (II) than in cyanocarboxylate (V). The same trend is indicated by Hammett substituent parameters σ_I, σ_R and σ^- for these substituents (Page & Williams, 1997), though these are derived from aromatic systems.

Experimental

Substance (V) was prepared by refluxing 8-dimethylaminonaphthalene-1-carbaldehyde (0.5 g, 2.5 mmol), ethyl cyanoacetate (0.68 g, 6 mmol), benzoic acid (0.2 g) and piperidine (2 ml) in toluene (50 ml) using a Dean Stark apparatus for 24 h. After extraction with aqueous sodium hydrogen carbonate and water, drying with sodium sulfate and evaporation, the residue was purified by chromatography on silica eluting with a 2:1 mixture of hexane and ethyl acetate to give (V) (0.24 g, 32%, m.p. 335–337 K).

Crystal data

$C_{18}H_{18}N_2O_2$
$M_r = 294.34$
Triclinic, $P\bar{1}$
$a = 8.3856$ (4) Å
$b = 9.7270$ (4) Å
$c = 11.1860$ (5) Å
$\alpha = 69.274$ (3)°
$\beta = 68.037$ (3)°
$\gamma = 70.933$ (3)°
$V = 771.31$ (6) Å^3
$Z = 2$
$D_x = 1.267$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11581 reflections
$\theta = 2.64$–23.65°
$\mu = 0.084$ mm^{-1}
$T = 150$ (2) K
Plate, yellow
0.3 × 0.3 × 0.1 mm

Table 1

Selected geometric parameters (Å, °).

O1—C14	1.198 (2)	N1—C18	1.459 (2)
O2—C14	1.328 (2)	N1—C19	1.459 (2)
O2—C15	1.457 (2)	N2—C13	1.143 (2)
N1—C1	1.432 (2)		
C14—O2—C15	116.55 (14)	N2—C13—C12	178.6 (2)
C1—N1—C18	112.84 (14)	O1—C14—O2	124.3 (2)
C1—N1—C19	114.89 (15)	O1—C14—C12	123.8 (2)
C18—N1—C19	112.5 (2)	O2—C14—C12	111.91 (14)

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan using multiple and symmetry-related data measurements *via SORTAV* (Blessing, 1995)
$T_{\min} = 0.912$, $T_{\max} = 0.992$
11 581 measured reflections
3134 independent reflections
2461 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 26.35°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.158$
$S = 1.064$
2939 reflections
272 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0865P)^2 + 0.2090P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.027$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.053 (10)

Table 2

Selected molecular geometry (Å, °) for compounds (II), (III) and (V).

	(II)	(III)	(V)
N1···C11	2.413 (2)	2.679 (2)	2.531 (2)
C11—C12	1.354 (2)	1.341 (2)	1.346 (2)
N1—C1—C2	124.3 (2)	122.3 (2)	123.3 (2)
N1—C1—C10	115.9 (1)	118.3 (2)	116.8 (1)
C1—C10—C8	120.4 (1)	123.5 (2)	122.4 (1)
C10—C8—C11	120.2 (1)	122.5 (2)	121.7 (1)
C7—C8—C11	120.3 (1)	117.6 (2)	118.6 (2)
N1—C11—C12	112.5 (1)	118.0 (1)	114.4 (1)
C18—N1—C1—C2	−81.5 (2)	−105.0 (2)	−82.9 (2)
C19—N1—C1—C2	49.2 (2)	25.9 (3)	47.9 (2)

H atoms were located and refined. C—H distances were in the range 0.92 (2)–1.08 (2) Å.

Data collection, cell refinement and data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1575). Services for accessing these data are described at the back of the journal.

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