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Structure from a Twinned Crystal of the Triclinic Form of the 1:1 Complex between *N,N*-Dimethylaniline and Hexafluorobenzene [$C_8H_{11}N.C_6F_6$] at 120 K

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Abstract. $M_r = 307.24$, triclinic, $P\bar{1}$, $a = 6.780$ (3), $b = 8.256$ (3), $c = 12.327$ (3) Å, $\alpha = 99.47$ (2), $\beta = 92.01$ (3), $\gamma = 106.04$ (3)°, $V = 651.7$ (4) Å³, $Z = 2$, $D_x = 1.566$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.167$ mm⁻¹, $F(000) = 312$, $T = 120$ K, $R = 0.060$ for 1581 observed non-overlapping reflections. The molecules are stacked alternately in infinite columns. Although the N atom has a partially tetrahedral geometry, the overlap between adjacent molecules is approximately equal on both sides of the dimethylaniline molecule, indicating that it is a π donor. The corresponding mean interplanar distances are 3.382 (2) and 3.392 (2) Å.

Introduction. In the monoclinic room-temperature form of the title compound, *N,N*-dimethylaniline (DMA) is situated on a twofold axis and it has therefore been concluded that the geometry of the N atom is planar, and that DMA is a π donor in this complex (Dahl, 1977). As, however, the observed thermal vibrations are large, this twofold symmetry may also be a result of orientational disorder. In the complex with tetrafluoro-*p*-benzoquinone the tetrahedral geometry of the N atom and the large differences in intermolecular distances on different sides of the molecule indicate that DMA is an n donor (Dahl, 1981). The present low-temperature study was initiated in order to elucidate the nature of DMA as an electron donor in the complex with hexafluorobenzene (HFB).

Experimental. Crystals formed by mixing equimolar amounts of the components. Unstable on exposure to atmosphere at room temperature. After sealing in capillaries at low temperature, large crystals grown by sublimation at room temperature. Crystal used for data collection $0.5 \times 0.5 \times 0.5$ mm.

With transformation matrix $(111/13\bar{1}/\bar{1}00)$, the triclinic cell may be transformed to a pseudo-monoclinic cell similar to that of the room-temperature form, but with the a and b axes doubled. There is thus a pseudo-mirror plane $(01\bar{1})$ in the cell, and twins of the pseudo-merohedral type (Cahn, 1954) with an obliquity of only 0.7° were formed when the crystals were cooled below the transition point. Overlap may occur for reflections from different individuals with indices related by the matrix $A = (100/\bar{1}\bar{1}\bar{1}/\bar{1}\bar{1}\bar{1})$ and consequently only for reflections with $h + k + l = 2n$.

Enraf–Nonius CAD-4 diffractometer and cooling device, unit-cell parameters and orientation matrix from setting angles of 25 reflections ($6 < \theta < 20^\circ$) with $h + k + l = 2n + 1$. Intensity collection by $\omega/2\theta$ scan, $\theta_{\max} = 28^\circ$, $0 \leq h \leq 8$, $-9 \leq k \leq 9$, $-14 \leq l \leq 14$. 3 standard reflections, no systematic decay, but two sharp falls down to 75%, probably due to ice formation. No absorption correction. 2294 unique reflections measured, 378 unobserved [$I < 2\sigma(I)$]. From all observed reflections non-H atoms located from a Patterson map, but least-squares refinement could not bring R below 0.15. 323 reflections with F_o considerably greater than F_c , and $F_c(hkl) \leq F_c(h'k'l')$, $h'k'l'$ related to hkl by A , were assumed to be affected by overlap and left out in subsequent refinement. 12 reflections, apparently influenced by ice formation indicated by standard reflections, were also left out. In last stage of refinement all H atoms located from difference map. Positional parameters for all atoms and thermal parameters, anisotropic for non-H atoms, isotropic for H atoms, refined. Final $R = 0.060$, $wR = 0.087$, goodness of fit $S = 1.16$, $w - 1$ for $|F_{\text{obs}}| \leq 8$ else $w = (8/|F_{\text{obs}}|)^2$. Max. $\Delta/\sigma = 0.09$. Max. and min. electron densities in final difference map 0.39 and -0.29 e Å⁻³. Table 1 gives atomic coordinates and Fig.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)

E.s.d.'s are in parentheses.
 $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$

	x	y	z	U_{eq}
F(1)	8801 (3)	5485 (2)	1358 (2)	382 (6)
F(2)	7804 (3)	2329 (3)	65 (2)	440 (7)
F(3)	6852 (3)	-506 (2)	988 (2)	402 (6)
F(4)	6927 (3)	-195 (2)	3221 (2)	370 (6)
F(5)	7956 (3)	2965 (3)	4521 (1)	410 (6)
F(6)	8868 (3)	5790 (2)	3591 (2)	383 (6)
C(1)	8350 (4)	4091 (4)	1811 (3)	292 (9)
C(2)	7843 (4)	2497 (4)	1160 (2)	291 (9)
C(3)	7353 (4)	1062 (4)	1632 (3)	281 (9)
C(4)	7391 (4)	1212 (4)	2761 (3)	271 (9)
C(5)	7910 (4)	2809 (4)	3411 (2)	280 (9)
C(6)	8378 (4)	4247 (4)	2946 (3)	286 (9)
C(7)	3877 (5)	5444 (4)	1824 (3)	358 (10)
C(8)	3289 (5)	3843 (4)	1148 (3)	320 (9)
C(9)	2759 (4)	2373 (4)	1615 (2)	275 (9)
C(10)	2759 (4)	2460 (4)	2747 (3)	258 (8)
C(11)	3348 (4)	4099 (4)	3427 (3)	286 (9)
C(12)	3879 (5)	5556 (4)	2955 (3)	317 (9)
C(13)	1722 (6)	-652 (4)	2496 (3)	357 (10)
C(14)	2476 (6)	1109 (5)	4372 (3)	384 (11)
N(1)	2163 (5)	995 (3)	3207 (2)	354 (9)

1 bond distances and angles.* Scattering factors of Stewart, Davidson & Simpson (1965) for H atoms and of Cromer & Mann (1968) for non-H atoms. Computer program for data reduction written at the University of Lund, modified at the University of Tromsø. Other programs used: XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. For the 656 reflections with $h + k + l = 2n$ not left out of the final refinement $R = 0.065$, which indicates some effect of overlap from the other individual of the twin.

The C—F bond distances observed in HFB are longer and the C—C distances shorter than those calculated and determined by experiment for the free molecule (Boggs, Pang & Pulay, 1982, and references therein), but the differences are not clearly significant. There are no significant deviations from planarity either of HFB or of the benzene ring of DMA, but N(1), C(13) and C(14) are -0.037 (3), 0.061 (4) and 0.163 (4) Å, respectively, out of the least-squares plane of this ring. The N atom has thus a partially tetrahedral geometry and the apparent twofold symmetry of DMA in the monoclinic form is probably a result of disorder.

The molecular packing (Fig. 2) is very similar to that in the monoclinic form. As a result of the phase transition, however, the two orientations of DMA are

arranged in an ordered way, whereas they are disordered and related by a mirror plane in the monoclinic form.

The planes of adjacent molecules in the stack make an angle of 1.8° with each other. Their separations, defined as the separations of the ring centres projected onto the mean-plane normal, are 3.382 (2) and 3.392 (2) Å on the two sides of each molecule, 0.13 – 0.14 Å shorter than in the monoclinic form. The H(9)···F(1) distance of 2.70 Å (Fig. 2b) is regarded as

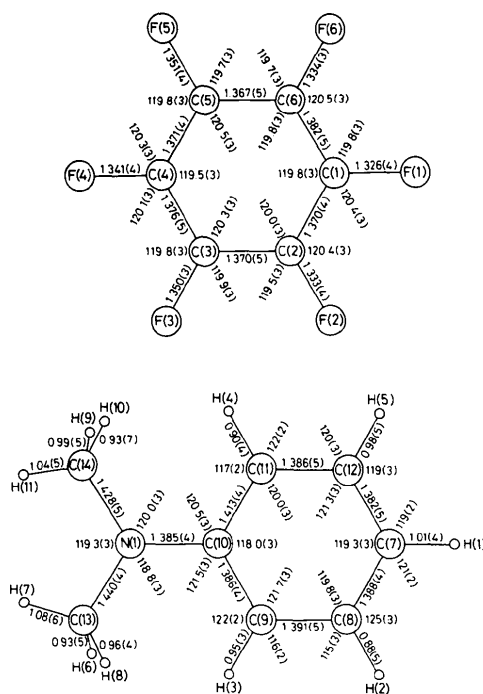


Fig. 1. Bond distances (Å) and angles ($^\circ$). E.s.d.'s are given in parentheses.

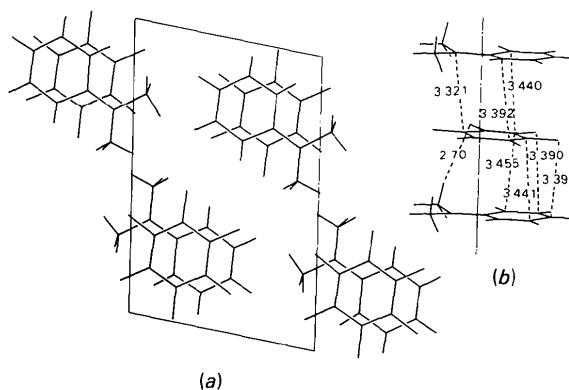


Fig. 2. The molecular packing viewed (a) along [100] and (b) perpendicular to [100]. Some intermolecular distances (Å) along the stack are given. E.s.d.'s ~ 0.004 Å (0.05 Å when H is involved).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42059 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

short, considering the observed C(14)—H(9) distance of 0.99 Å and the non-spherical shape of the F atom (Nyburg, 1979). No intermolecular distances between different stacks are shorter than the van der Waals distance.

The tetrahedral character of N is less pronounced than in the complex with tetrafluoro-*p*-benzoquinone and seems to have a much smaller effect on the molecular packing. The sum of bond angles around N is 347.9° in the tetrafluoro-*p*-benzoquinone complex and 358.1° in this complex. The interplanar distances on different sides of DMA differ by 0.22 Å in the tetrafluoro-*p*-benzoquinone complex and only 0.01 Å in this complex. The molecules overlap very differently on different sides in the tetrafluoro-*p*-benzoquinone complex. In this complex the mean plane normal of the molecules makes an angle of only 2.7° with the *a* axis

and the overlap on both sides is thus approximately as shown in Fig. 2(a). It seems still reasonable therefore to conclude that DMA is a π donor rather than an *n* donor in this complex.

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Méthyl-4 (Propyn-2 yloxy)-7 Chroménone-2 (Giparmène), C₁₃H₁₀O₃

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Abstract. $M_r = 214.2$, orthorhombic, $P2_12_12_1$, $a = 10.99$ (2), $b = 23.46$ (1), $c = 4.001$ (1) Å, $V = 1032$ (2) Å³, $Z = 4$, $D_m = 1.38$ (3), $D_x = 1.378$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.092$ mm⁻¹, $F(000) = 448$, $T = 294$ (1) K, $R = 0.027$ for 831 independent reflections [$I > 3\sigma(I)$]. The interatomic distances and bond angles of the coumarinic group are in good agreement with published values for other coumarinic compounds. The relatively short acetylenic bond could indicate an important terminal H mobility. The two rings are planar, with a dihedral angle between their planes of approximately 1°.

Introduction. Selon Astoin, Lepage & Poisson (1984), la méthyl-4 (propyn-2 yloxy)-7 chroménone-2 présente une activité analgésique importante qui permet d'envisager son emploi en thérapeutique. Son étude par diffraction X a été entreprise dans le but de préciser la géométrie de sa molécule et d'établir d'éventuelles

relations entre celle-ci et les propriétés antalgiques. Le produit utilisé nous a été fourni gracieusement par les Laboratoires Biocodex. Il contenait des cristaux parmi lesquels ont été prélevés les échantillons choisis pour réaliser l'étude structurale.

Partie expérimentale. Cristal approximativement cubique de 0,26 mm d'arête. Mesure de la masse volumique par flottaison. Diffractomètre Enraf-Nonius CAD-4. Dimensions de la maille élémentaire déterminées sur monocristal avec 25 réflexions telles que $5,41 \leq \theta \leq 12,67^\circ$. Pas de correction d'absorption. $0,037 \leq (\sin\theta)/\lambda \leq 0,661$ Å⁻¹. $0 \leq h \leq 14$, $0 \leq k \leq 31$, $0 \leq l \leq 5$. Réflexions de contrôle des intensités: 14 $\bar{1}$, 13 $\bar{1}$ et 170. Variation de I : 0,4%, $\sigma(I)/I = 0,003$. 1510 réflexions indépendantes mesurées. 679 réflexions inobservées [$I \leq 3\sigma(I)$]. Méthodes directes, programme MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Affinement sur F ,