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Structure of the 4:1 Inclusion Compound between Deoxycholic Acid and (*E*)-*p*-Dimethylaminoazobenzene

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(Received 24 March 1982; accepted 27 April 1982)

Abstract

The title compound, $4\text{C}_{24}\text{H}_{40}\text{O}_4 \cdot \text{C}_{14}\text{H}_{15}\text{N}_3$, $M_r = 1795.6$, crystallizes in space group $P2_12_12_1$ with $a = 25.676$ (8), $b = 13.731$ (3), $c = 7.160$ (2) Å, $V = 2524.3$ Å³, $Z = 4$, $D_m = 1.17$, $D_x = 1.18$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 4.3$ mm⁻¹ (m.p. 479–480 K). The structure has been refined to $R = 0.09_3$ and $R_w = 0.09$, for 1810 observed reflections with $I > 2\sigma(I)$. The crystal packing is characterized by an assembly of pleated antiparallel bilayers, nearly equal to that of the acetophenone–choleic acid complex, which give rise to canals filled by *p*-dimethylaminoazobenzene molecules. The guest molecules, located by van der Waals energy calculations, run along *c* and have their long

axes approximately parallel to *c*. The C(5), C(6), C(19), C(20), C(21) and C(22) atoms, together with their H atoms, are engaged in strong interactions with the atoms of *p*-dimethylaminoazobenzene.

Introduction

The bile acid 3 α ,12 α -dihydroxy-5 β -cholan-24-oic acid (deoxycholic acid, DCA) gives rise to host lattices of the 'canal' type in which several guest components can be accommodated, especially in the orthorhombic phases (D'Andrea, Fedeli, Giglio, Mazza & Pavel, 1981; Giglio, 1981, and references therein). In order to throw light on the possibilities of formation of the DCA

canal complexes and on the nature and strength of the host-guest interactions we have decided to solve other crystal structures besides those already known and to undertake potential-energy calculations (Candeloro De Sanctis & Giglio, 1979) and enthalpy-change measurements (Ferro, Quagliata, Giglio & Piacente, 1981). This paper deals with the inclusion compound (DCADAB) formed by the carcinogenic (*E*)-*p*-dimethylaminoazobenzene (DAB) and DCA. DAB was one of the aminoazo dyes studied by Cilento (1951, 1952) in combination with DCA by means of phase-equilibrium diagrams. He was unable to establish the DCA:DAB ratio, although he advanced the hypothesis that the ratio could be 4. Furthermore, the high melting point and the relatively short *a* axis of DCADAB, if compared with those of other choleic acids occluding aromatic hydrocarbons (Giglio, 1981; Ferro, Quagliata, Giglio & Piacente, 1981), supported the presence of strong host-guest interactions, so that it was judged interesting to determine which atoms are engaged in the DAB-DCA binding. On the other hand, the *a* and *c* values suggest that DCADAB belongs to the α structures of the orthorhombic choleic acids (Candeloro De Sanctis & Giglio, 1979) and populates the *A* minimum region characterized by guest molecules of small size or thread-like, non-aromatic (except acetophenone) (Popovitz-Biro, Chang, Tang, Shochet, Lahav & Leiserowitz, 1980).

Experimental

DCADAB was prepared by adding the azo dye to a hot ethanolic solution of DCA. Prismatic orange crystals were obtained by slow evaporation.

The composition of DCADAB was checked by density measurements and ¹H NMR. The observed density was obtained by flotation in *n*-hexane and carbon tetrachloride and agrees with a DCA:DAB ratio of 4. The same ratio was given by NMR with (CD₃)₂SO as solvent.

A crystal elongated along *c*, with dimensions 0.7 × 0.3 × 0.2 mm, was used to determine the cell constants from a least-squares refinement performed on 13 reflections and to collect intensities within the range 1.5 ≤ 2θ ≤ 60° on a Syntex P₂₁ automated diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$). The data were recorded by the ω -scan mode at a scan rate within the range 1.0 to 29.3° min⁻¹, depending on the peak intensity, with a scan width of 1.3°. Three reflections, selected for orientation control and measured every 100 reflections, remained essentially constant throughout the run. Backgrounds were estimated by stationary counting for half the scan time. Lorentz and polarization corrections were applied taking into account the monochromator crystal (Azaroff, 1955). Corrections for the

anisotropy of the absorption, due to the shape of the crystal, were applied.

Structure determination and refinement

The structure was solved by means of the minimum residual method, assuming the same atomic coordinates for DCA as those found in the palmitic acid-choleic acid (DCAPAL) complex (Coiro, D'Andrea & Giglio, 1980). Firstly *R* was computed as a function of the DCA translational degrees of freedom, neglecting the contribution of DAB, for reflections with $\sin \theta/\lambda \leq 0.30 \text{ \AA}^{-1}$. The DCA molecule, treated as a rigid body, gave the best *R* with the orientation found in DCAPAL and with a 0.4 Å translation along *b*. Subsequently *R* strongly decreased when a rigid planar DAB molecule was introduced with a geometry (Fig. 1) derived from the bond distances and angles observed in other azobenzene structures (Brown, 1966*a,b*; Hope & Victor, 1969; Hanson, 1973; Kurosaki, Kashino & Haisa, 1976). As in other orthorhombic choleic acids the contribution of the guest molecule is significant only for the *hk0* reflections. Therefore, we determined the orientation and the translations along *a* and *b* of DAB to a good approximation, whereas we were unable to establish the translation along *c*.

Isotropic full-matrix least-squares refinement was carried out only for the DCA molecule with *SHELX* (Sheldrick, 1976), using the scattering factors of Cromer & Mann (1968) and the weighting scheme $w = K_1/[1\sigma^2(F_o) + K_2F_o^2]$, K_1 and K_2 being two constants redetermined after each cycle. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The final *R* was 0.15. At this stage a difference synthesis showed many peaks, three of which could be attributed to three atoms of the 'best' DAB, obtained in the minimum residual analysis, having nearly equal *x* and *y* coordinates and Δz . Further full-matrix cycles were calculated including DAB, treated isotropically as a rigid body, with fixed *B*'s of 8 Å² and occupancy factor of 0.25, while anisotropic thermal parameters were applied to the DCA atoms. The DAB molecule was rotated around three perpendicular axes passing through the point halfway between N(43) and N(44). The H atoms of

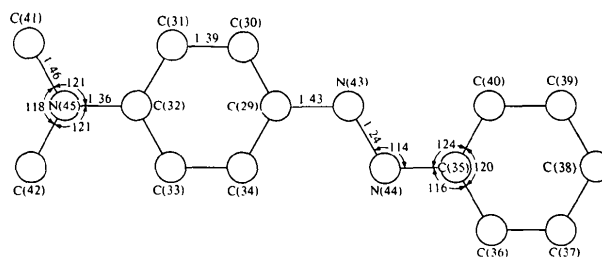


Fig. 1. Atomic numbering and bond distances (Å) assumed for DAB.

DCA were generated at the expected positions, except those of the hydroxyl and carboxyl groups. Their B^s (5 \AA^2) and positional parameters were kept fixed. Unfortunately, the refinement did not converge, owing to the ill-conditioned parameters of DAB. Thus, it was decided to resort to van der Waals energy calculations (Candeloro De Sanctis, 1982) using potentials previously verified (Pavel, Quagliata & Scarcelli, 1976). The DCA atomic coordinates were those corresponding to $R = 0.15$. The H atoms of DAB were generated in the molecular plane with C–H bond distances of 1.08 \AA and $\angle \text{H–C–C}$ bond angles of 120° . The methyl group was treated as one atom. The potential energy was computed as a function of three rotational and three translational degrees of freedom of DAB, which was moved as a rigid body. All the interactions between a central DAB molecule, on one hand, and the 20 nearest DCA molecules covering the interior surface of the canal together with the two DAB molecules immediately adjacent to the central one, on the other, were computed with a cut-off distance of 7 \AA . The parametric space was completely explored and just one very sharp minimum was located. The atomic coordinates of DAB corresponding to this minimum, reported in Table 1, were introduced in a new refinement which converged to a final R and R_w of 0.09_3 and

0.09 , respectively. The final atomic coordinates are reported in Table 2.*

The bond lengths and angles of DCA are shown in Figs. 2 and 3. Their average e.s.d.'s are 0.011 \AA and

* Lists of structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36919 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for the non-H atoms of DCADAB with their e.s.d.'s in parentheses

$$U_{\text{eq}} \text{ is defined as } U_{\text{eq}} = (U_{11} U_{22} U_{33})^{1/3}.$$

	x	y	z	U_{eq}
C(1)	1221 (4)	2833 (6)	1399 (13)	50 (5)
C(2)	679 (4)	3143 (6)	2003 (12)	51 (5)
C(3)	724 (4)	3843 (6)	3615 (15)	56 (5)
C(4)	1023 (3)	3405 (6)	5237 (12)	43 (5)
C(5)	1571 (3)	3061 (6)	4637 (12)	47 (5)
C(6)	1871 (3)	2622 (6)	6281 (14)	55 (6)
C(7)	1655 (4)	1618 (6)	6843 (13)	55 (6)
C(8)	1634 (3)	896 (5)	5220 (12)	44 (5)
C(9)	1320 (3)	1349 (5)	3613 (12)	35 (4)
C(10)	1545 (3)	2357 (5)	2938 (12)	43 (5)
C(11)	1238 (3)	601 (6)	2048 (12)	45 (5)
C(12)	992 (3)	-353 (5)	2711 (11)	38 (4)
C(13)	1314 (3)	-797 (5)	4245 (12)	37 (4)
C(14)	1381 (3)	-40 (5)	5798 (11)	41 (4)
C(15)	1618 (4)	-619 (6)	7417 (13)	57 (6)
C(16)	1369 (4)	-1626 (6)	7291 (12)	55 (6)
C(17)	1070 (3)	-1652 (5)	5414 (12)	42 (5)
C(18)	1839 (3)	-1140 (6)	3407 (13)	49 (5)
C(19)	2101 (3)	2200 (7)	2127 (15)	54 (5)
C(20)	1059 (3)	-2704 (5)	4593 (14)	43 (5)
C(21)	787 (4)	-2784 (6)	2691 (14)	57 (6)
C(22)	851 (4)	-3446 (6)	5981 (13)	53 (5)
C(23)	293 (4)	-3304 (6)	6584 (15)	64 (6)
C(24)	92 (4)	-4114 (7)	7812 (15)	63 (6)
O(25)	205 (2)	4087 (5)	4216 (11)	71 (4)
O(26)	462 (2)	-177 (4)	3359 (8)	48 (3)
O(27)	109 (4)	-4955 (5)	7388 (13)	106 (7)
O(28)	-80 (3)	-3823 (4)	9411 (10)	64 (4)
C(29)	2535 (6)	4934 (13)	-3179 (28)	
C(30)	2916 (6)	4514 (13)	-2059 (28)	
C(31)	2876 (6)	4569 (13)	-126 (28)	
C(32)	2455 (6)	5043 (13)	687 (28)	
C(33)	2074 (6)	5462 (13)	-433 (28)	
C(34)	2114 (6)	5407 (13)	-2366 (28)	
C(35)	2336 (6)	5131 (13)	-8071 (28)	
C(36)	1955 (6)	5551 (13)	-9191 (28)	
C(37)	1995 (6)	5496 (13)	-11124 (28)	
C(38)	2417 (6)	5022 (13)	-11937 (28)	
C(39)	2798 (6)	4603 (13)	-10817 (28)	
C(40)	2758 (6)	4658 (13)	-8884 (28)	
C(41)	2811 (6)	4661 (13)	3784 (28)	
C(42)	1977 (6)	5589 (13)	3465 (28)	
N(43)	2610 (6)	4841 (13)	-5151 (28)	
N(44)	2262 (6)	5224 (13)	-6100 (28)	
N(45)	2416 (6)	5096 (13)	2578 (28)	

Table 1. Fractional atomic coordinates ($\times 10^4$) of DAB corresponding to the van der Waals energy minimum

The H atoms have the same numbering as the C atoms to which they are bonded.

	x	y	z
C(29)	2565	4929	-2746
C(30)	2908	4384	-1669
C(31)	2922	4509	257
C(32)	2593	5180	1106
C(33)	2249	5725	29
C(34)	2235	5599	-1897
C(35)	2280	5071	-7590
C(36)	1936	5616	-8666
C(37)	1922	5490	-10592
C(38)	2251	4820	-11441
C(39)	2595	4275	-10364
C(40)	2609	4401	-8438
C(41)	2964	4739	4150
C(42)	2264	6002	3913
N(43)	2578	4750	-4712
N(44)	2266	5250	-5623
N(45)	2606	5303	2990
H(30)	3164	3863	-2328
H(31)	3189	4086	1094
H(33)	1993	6246	688
H(34)	1968	6023	-2733
H(36)	1680	6137	-8007
H(37)	1655	5914	-11429
H(38)	2241	4723	-12937
H(39)	2851	3754	-11024
H(40)	2876	3977	-7602

0.7° with maximum values of 0.013 Å and 0.9°. Schematic drawings of the crystal packing and of a bilayer viewed along *c* and *a* respectively are visible in Figs. 4 and 5.

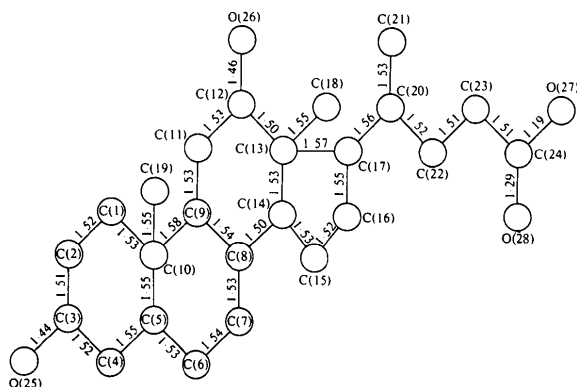


Fig. 2. Bond lengths (Å) of DCA.

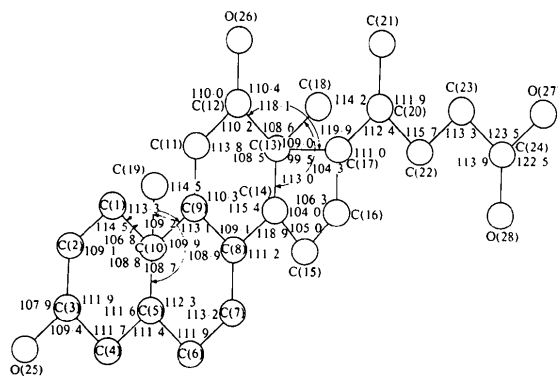


Fig. 3. Bond angles (°) of DCA.

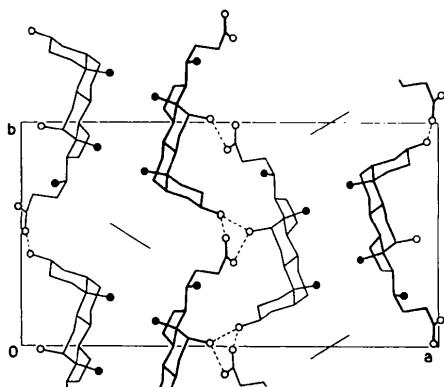


Fig. 4. DCADAB crystal packing viewed along *c*. The filled and open circles are methyl groups and oxygen atoms respectively. The line passing near to (*a*/*b*) represents the projection of the DAB molecular plane. The broken lines indicate hydrogen bonds.

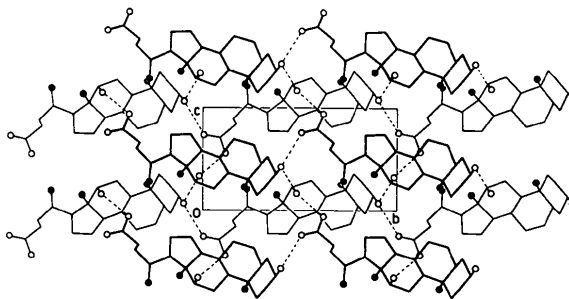


Fig. 5. DCADAB bilayer viewed along *a*. The symbols have the same meaning as in Fig. 4.

Table 3. Torsion angles (°) of the DCA side chain and ring *D* in DCADAB together with Δ and φ_m

The e.s.d.'s are in parentheses.

C(13)–C(17)–C(20)–C(22)	175.2 (7)	C(13)–C(14)	45.4 (7)
C(17)–C(20)–C(22)–C(23)	63.2 (10)	C(14)–C(15)	–35.0 (9)
C(20)–C(22)–C(23)–C(24)	174.4 (8)	C(15)–C(16)	9.5 (9)
C(13)–C(17)–C(20)–C(21)	–56.1 (10)	C(16)–C(17)	18.6 (9)
C(16)–C(17)–C(20)–C(21)	–177.8 (7)	C(13)–C(17)	–39.0 (7)
C(21)–C(20)–C(22)–C(23)	–66.7 (10)	Δ	11
C(22)–C(23)–C(24)–O(27)	–53.9 (14)	φ_m	46
C(22)–C(23)–C(24)–O(28)	123.1 (9)		

Discussion

The DCA bond distances and angles are in satisfactory agreement with those observed in other choleic acid crystal structures [see Giglio (1981) for references]. The relevant dihedral angles of the side chain and ring *D*, together with the phase angle of pseudorotation Δ and the maximum torsion angle φ_m (Altona, Geise & Romers, 1968) are listed in Table 3 according to the convention of Klyne & Prelog (1960). The side-chain conformation is *gauche* as in other orthorhombic (Giglio, 1981) and tetragonal (Coiro, D'Andrea & Giglio, 1979) phases and is coupled with the half-chair symmetry approached by the *D* ring (Giglio & Quagliata, 1975).

The crystal packing (Fig. 4) is very similar to that of the palmitic acid–choleic acid complex (Coiro, D'Andrea & Giglio, 1980) both in terms of the structure of the pleated bilayers (Fig. 5), belonging to the α group of choleic acids (Candeloro De Sanctis & Giglio, 1979), and in terms of the shape and size of the canal section ($\sim 5.5 \times 2.8$ Å), which are determined by the assembly of adjacent bilayers. The bilayer is mainly stabilized by an efficient network of hydrogen bonds, whose repeat unit along *c* is reported in Table 4, and protrudes a non-polar outer surface towards the central region of the canal.

The molecular plane of DAB nearly coincides with that passing through the C atoms of the palmitic acid. These two molecules are sandwiched in canals of rectangular section with the two longer edges mainly occupied by *A* rings and C(6) methylenic groups and

Table 4. O...O distances (Å) of the hydrogen bonds in a bilayer

The e.s.d.'s are within the range 0.009–0.012 Å.

O(25)...O(27ⁱ) 2.64 O(28ⁱ)...O(26ⁱⁱ) 2.64 O(26ⁱⁱ)...O(25ⁱⁱⁱ) 2.71

Symmetry code: (i) $x, 1 + y, z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, y, 1 + z$.

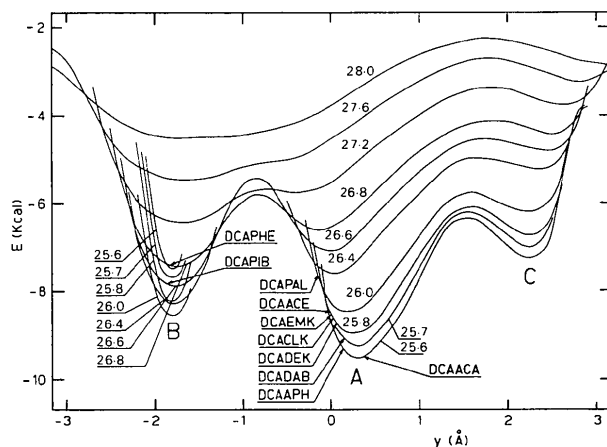


Fig. 6. Curves of the van der Waals energy vs y , translation of the bilayer along b , at different values of a for the α structures. The arrows show the positions corresponding to the experimental crystal structures. (1 kcal \equiv 4.18 kJ.)

the two shorter ones by side chains. The opposite edges are related by a 2_1 axis parallel to c and passing through $(a/4, b/2)$. The section of the canal in DCADAB is the smallest together with those of the choleic acids containing acetic and palmitic acid, acetone, acetophenone, chloroacetone, ethyl methyl ketone and diethyl ketone, which populate the A minimum region of the α structures (Candeloro De Sanctis & Giglio, 1979). The position of DCADAB is shown in Fig. 6 where the abbreviations used to indicate the choleic acids are explained in Giglio (1981). DCADAB is the second case, after that of the acetophenone-choleic acid (DCAAPH), of an aromatic molecule as guest component in a DCA canal complex located in the region A of the α group, characterized by the lowest values of a (~ 25.5 – 26.0 Å) assumed by the choleic acids investigated so far. On the other hand, DCADAB has a and b cell parameters very close to those of DCAAPH ($a = 25.59$, $b = 13.71$ Å; Tang, 1979) and nearly the same y , equal to 0.14 Å, so that it seems reasonable to suppose that the host-guest interactions would be similar.

The shortest interactions corresponding to the minimum-energy point (see Table 1 for DAB atomic coordinates) are given in Table 5. The minimum-energy DAB position is, in our opinion, more reliable than that found after the refinement, lying in the same region of

the deepest minimum, although they do not differ much in terms of both energy values and molecular arrangements (Fig. 7). By inspection of Table 5 it is clear that the strongest interactions between two DAB molecules adjacent in a canal are caused by the C(38)–H(38) group on the one hand and the aminomethyl groups on the other. Moreover, the phenyl ring containing the dimethylamino group and the $>C(35)-N(43)=N(44)$ fragment are firmly anchored to two H(5) atoms belonging to two DCA molecules related by the 2_1 axis and pointing towards the DAB molecular plane, so that it may be supposed that the main attraction between DCA and DAB is due to polarization bonding involving the π charge cloud of the guest component. Likewise in DCAAPH H(5) is engaged in good interactions with the keto group and can be abstracted, on UV irradiation, yielding an addition product at C(5) (Popovitz-Biro, Chang, Tang, Shochet, Lahav & Leiserowitz, 1980).

Table 5. The most relevant intermolecular contacts (Å) in the DCADAB packing of minimum energy

The H atoms have the same numbering as the C atom to which they are bonded.

DAB–DAB interactions

C(41)...C(38 ⁱ)	3.7	C(42)...C(38 ⁱ)	3.7
C(41)...H(38 ⁱ)	2.8	C(42)...H(38 ⁱ)	2.9

DAB–DCA interactions

C(29)...H(5 ⁱⁱ)	2.8	C(42)...C(20 ^{iv})	3.6
C(30)...H(5 ⁱⁱ)	2.8	C(42)...H(20 ^{vi})	2.6
C(30)...H(20 ⁱⁱⁱ)	2.7	C(42)...C(19 ^{vii})	3.8
C(31)...H(5 ⁱⁱ)	2.7	C(42)...C(6 ⁱⁱ)	3.5
C(31)...H(20 ⁱⁱⁱ)	2.8	C(42)...H(6 ⁱⁱ)	2.8
C(32)...H(5 ⁱⁱ)	2.7	N(43)...H(5 ^{iv})	2.6
C(32)...C(6 ⁱⁱ)	3.3	N(44)...H(5 ^{iv})	2.5
C(33)...H(5 ⁱⁱ)	2.7	N(45)...H(6 ⁱⁱ)	2.6
C(33)...C(6 ⁱⁱ)	3.3	H(30)...H(20 ⁱⁱⁱ)	2.0
C(33)...H(6 ⁱⁱ)	2.7	H(31)...C(22 ⁱⁱⁱ)	2.6
C(34)...H(5 ⁱⁱ)	2.8	H(31)...H(22 ⁱⁱⁱ)	2.2
C(34)...C(19 ⁱⁱⁱ)	3.5	H(36)...H(20 ⁱⁱⁱ)	2.2
C(35)...H(5 ^{iv})	2.6	H(36)...C(21 ^{viii})	2.8
C(38)...H(6 ^v)	2.7	H(37)...H(22 ^{iv})	2.0
C(39)...C(19 ^{iv})	3.6	H(37)...C(22 ^{iv})	2.9
C(40)...C(19 ^{iv})	3.3	H(39)...H(20 ^v)	2.1

Symmetry code: (i) $x, y, 2 + z$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (iv) $x, y, z - 1$; (v) $x, y, z - 2$; (vi) $x, 1 + y, z$; (vii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (viii) $x, 1 + y, z - 1$; (ix) $x, 1 + y, z - 2$; (x) $\frac{1}{2} - x, -y, z - \frac{1}{2}$.

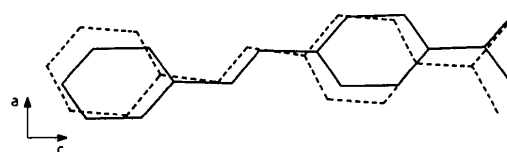


Fig. 7. Projection on the ac plane of the DAB molecule corresponding to the energy minimum (full line) and to the situation obtained at the end of the refinement (broken line).

The C(6) methylenic group is exposed to the —C(33)—C(32)—N(45)—C(42) moiety and is confirmed as a potentially reactive site, whereas the C(19) methyl groups, belonging to a pair of DCA related by the 2_1 axis, each interact with a different phenyl ring. The outer H atoms of DAB point towards the side chains of DCA and form good contacts with all the atoms except that with the terminal methylenic and carboxyl groups. In this connection we should remember the ability of DCA to change by about 80° the orientation of the guest molecular plane with respect to the *A* rings and to the side chains, as in the case of the phenanthrene and *p*-diiodobenzene choleic acids (Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1972) populating the *B* minimum region of Fig. 6. Thus, the most probable candidates as photoaddition sites may become C(15) and C(16).

The Central Services of the CNR Research Area of Rome are thanked for the NMR spectra. Two of the authors (EG and GP) acknowledge financial support from the Consiglio Nazionale delle Ricerche.

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Acta Cryst. (1982). **B38**, 2620–2625

Electron Density Distribution in Thiourea. Comparison with the Urea Molecule

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(Received 30 January 1981; accepted 21 September 1981)

Abstract

The electron density distribution in thiourea has been refined using a multipolar expansion, and a comparison is made with the urea molecule [Mullen (1980), *Acta Cryst.* **B36**, 1610–1615]. An analysis is made of the errors arising from attributing phases from $F_{c,n}$ to the observed structure amplitudes and the model-dependency of these errors is discussed.

Introduction

Initial work on thiourea has been reported by Mullen & Hellner (1978). X-ray data were measured at 123 K and full experimental details are reported in the above reference.

Previous work on urea has already been reported. Scheringer, Mullen, Hellner, Hase, Schulte & Schweig (1978) have carried out a study of urea in which the