

Intermolecular interactions and molecular geometry in molecular complexes of *N,N*-dimethylaniline: the 1:1 complex with 1,2,4,5-tetracyanobenzene

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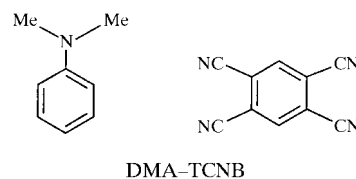
The partner molecules of *N,N*-dimethylaniline–1,2,4,5-tetracyanobenzene (1/1), $C_8H_{11}N \cdot C_{10}H_2N_4$, are stacked alternately in infinite columns. The N atom of the *N,N*-dimethylaniline molecule has a partially tetrahedral character and the distance between neighbouring molecules in the stack is relatively short on the side where the lone-pair electrons of this atom are located. Molecular-packing analysis of this and three other complexes of *N,N*-dimethylaniline shows that there is a close relationship between the strength of the intermolecular interaction on this side and the tetrahedral character of the N atom.

Comment

In the molecular complex between *N,N*-dimethylaniline (DMA) and fluoranil (FA), the N atom of the DMA molecule has a partially tetrahedral character, and the distance between neighbouring molecules in the stack is very short on the side of the DMA molecule where the lone-pair electrons of this atom are located (Dahl, 1981). It has been confirmed by molecular-packing analysis that the intermolecular interaction on this side is exceptionally strong compared with the interactions in other complexes of FA (Dahl, 1998). This may be interpreted as a result of an $n-\pi^*$ charge-transfer interaction on this side. In the DMA complexes with 3,5-dinitro-1-cyanobenzene (DNCB) (Bock *et al.*, 1996) and with hexafluorobenzene (HFB) (Dahl, 1985), the corresponding N atom is closer to trigonal and the intermolecular distances in the stack indicate no strong influence of the lone pair. Relatively few examples are known where the geometry of a molecule is significantly changed as a result of charge-transfer complex formation. For complexes of 7,7,8,8-tetracyanoquinodimethane, however, a quantitative correlation between molecular geometry and degree of charge-transfer has been established (Flandrois & Chasseau, 1977).

The crystals of the DMA–FA complex are difficult to grow, very unstable, and the one used for the structure determina-

tion was very poor. The standard deviations of this structure, which was determined at room temperature, are thus relatively large. A redetermination at low temperature would have been desirable, but has proved to be difficult. Crystals of the DMA complex with 1,2,4,5-tetracyanobenzene (TCNB), which was expected to have a strength between those with FA and DNCB, can be cooled down without being damaged. The low-temperature structure of this complex, (I), was investigated in order to study more closely this kind of interaction and the relationship between this and the geometry of the amino group.



No significant change in geometry of the TCNB molecule as a result of the complex formation is observed. The geometry of the amino group of DMA is given in Table 1. The deviation from 360° of the sum of the bond angles around N1 may be used as a measure of its tetrahedral character. This sum is $353.2(3)^\circ$, significantly smaller than in the complex with DNCB, $358.3(3)^\circ$ and with HFB, $358.1(5)^\circ$, but larger, although probably not significantly, than in the complex with FA, $347.9(17)^\circ$.

As shown in Fig. 1, the partner molecules are stacked alternately in infinite columns. The angle between the plane of the TCNB molecule and the planar part of the DMA molecule is $6.3(1)^\circ$. The average distance between the planar parts of the molecules is 3.28 \AA on the lone-pair side and 3.38 \AA on the other side. The corresponding distances in the complex with FA are 3.24 and 3.46 \AA , in the complex with DNCB 3.42 and 3.53 \AA and in the complex with HFB 3.38 and 3.39 \AA . The shortest intermolecular N1...C distance in the stack in the title compound, to C18, is $3.099(3) \text{ \AA}$. The shortest N...C distance in the FA complex is $3.033(21) \text{ \AA}$, in the DNCB complex $3.378(3) \text{ \AA}$ and in the HFB complex $3.321(5) \text{ \AA}$.

A similar relationship between shortest N...C distance and geometry of amino groups has been observed for TCNB complexes with various N-methylated *p*-phenylenediamines (Ohashi, 1973). For these complexes, however, the geometries are not directly comparable, as the amino groups belong to different kinds of molecules, and some of them are unsubstituted. It is worth noticing that although these amines have lower ionization potentials than DMA (Lias *et al.*, 1998), the shortest N...C distances are longer than in the DMA complex with TCNB.

Different steric conditions in different complexes may have considerable effects on interplanar distances and intermolecular distances between individual atoms. A direct comparison of these distances is not very suitable in order to estimate the strength of the intermolecular interactions. In order to estimate this more quantitatively a molecular-packing analysis has been performed based on the atom-to-atom potential method, using the computer program *PCK83*

(Williams, 1983). Potential parameters for Buckingham potentials were those given by Williams & Houpt (1986). All C–H distances were adjusted to be 1.00 Å in these calculations, as the calculation of potential parameters for the H atoms was based on a slight foreshortening of the bond distance (Williams & Cox, 1984). Net atomic charges were calculated by the AM1 method (Dewar *et al.*, 1985), using the computer program GAUSSIAN94 (Frisch *et al.*, 1995). In this analysis, a lattice-energy minimization was performed, where only translation of the DMA molecule along the stack axis and variation of the lengths of the crystallographic axes were allowed. By this procedure, the molecular overlap in the stack was kept approximately unchanged. The interplanar distances in the minimum-energy structure obtained in this way should be those expected with this overlap if only ordinary van der Waals interactions were present. The increase in these distances relative to those in the experimental structure should give an indication of the strength of additional interactions, in this case probably mainly charge-transfer interactions. Similar calculations for various molecular complexes have been described earlier (Dahl, 1990, 1998).

The increase in interplanar distance by this procedure for the title complex was 0.21 Å on the lone-pair side and 0.11 Å on the opposite side of the DMA molecule. This indicates a weak π - π^* charge-transfer interaction on the opposite side and an additional n - π^* charge-transfer interaction on the lone-pair side. Similar calculations gave increases of 0.26 and 0.00 Å for the DMA–FA complex, 0.06 and 0.02 Å for the DMA–DNCB complex and 0.05 and 0.07 Å for the DMA–HFB complex on the lone-pair side and the opposite side, respectively. These values are not directly comparable, as the structure of the title complex was determined at 100 K, the FA complex at room temperature, the DNCB complex at 200 K and the HFB complex at 120 K. The decrease with increasing temperature in the values obtained for the opposite side may be explained mainly as an effect of the different thermal expansions in the experimental structures. The strength of the interaction on this side seems thus to be approximately the same in all these complexes. The difference between the values obtained for the two sides can then be regarded as a measure of the strength of the additional n - π^* interaction.

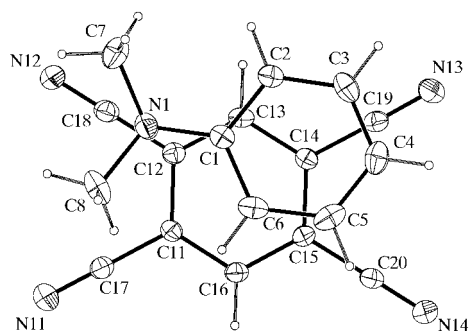


Figure 1

The title complex with the atom-labelling scheme showing 50% probability displacement ellipsoids viewed perpendicular to the average molecular plane.

This interaction is thus by far the strongest in the complex with FA, relatively strong also in that with TCNB, weaker in that with DNCB, whereas no such additional interaction seems to be present in the complex with HFB. As expected, the strength of the n - π^* interaction increases with increasing electron affinity of the acceptor molecule (Bartmess, 1998). There seems to be a strong correlation between the strength of this interaction and the geometry of the amino group, although this geometry in the DNCB complex is surprisingly equal to that in the HFB complex and more different than expected from that in the TCNB complex.

Experimental

N,N-Dimethylaniline and 1,2,4,5-tetracyanobenzene, both obtained from Fluka Chemie AG, were dissolved in acetone in the molar ratio 1:1. The complex was crystallized by evaporating the solvent at room temperature.

Crystal data

C₈H₁₁N·C₁₀H₂N₄
M_r = 299.33
 Triclinic, *P* $\bar{1}$
a = 7.325 (3) Å
b = 7.982 (4) Å
c = 13.452 (6) Å
 α = 74.44 (4)°
 β = 87.05 (3)°
 γ = 80.30 (3)°
V = 746.8 (6) Å³

Z = 2
D_x = 1.331 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 6.45–13.13°
 μ = 0.084 mm⁻¹
T = 100 (2) K
 Plate, brown
 0.45 × 0.35 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: Gaussian (PLATON; Spek, 1998)
T_{min} = 0.973, *T_{max}* = 0.988
 3648 measured reflections
 3603 independent reflections
 2501 reflections with *I* > 2 σ (*I*)

R_{int} = 0.040
 θ_{\max} = 27.98°
h = 0 → 9
k = -10 → 10
l = -17 → 17
 3 standard reflections
 frequency: 60 min
 intensity decay: 12%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.043
wR(*F*²) = 0.150
S = 1.066
 3603 reflections
 211 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 0.2695P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.013 (4)

Table 1

Selected geometric parameters (Å, °).

C1–N1	1.384 (2)	N1–C8	1.451 (2)
N1–C7	1.448 (2)		
C1–N1–C7	118.76 (15)	C7–N1–C8	115.22 (15)
C1–N1–C8	119.20 (15)		

All H atoms were located in a difference map. In the refinement, the H atoms were constrained to be in ideal positions and were allowed to ride on the C atoms to which they are attached.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1110). Services for accessing these data are described at the back of the journal.

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