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Molecular Complex of 2-[4-(Dimethylamino)phenylimino]-3-oxo-N-phenylbutanamide and N,N-Dimethyl-4-nitrosoaniline

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Abstract

2-[4-(Dimethylamino)phenylimino]-3-oxo-N-phenylbutanamide and N,N-dimethyl-4-nitrosoaniline form a molecular complex in which they are linked by a hydrogen bond and π–π* interactions. Intermolecular contacts shorter than 3.2 Å are also observed between adjacent complexes arranged in double layers. The geometry of the dimethylaminophenyl moiety in both molecules indicates a contribution from the *para*-quinonoid structure.
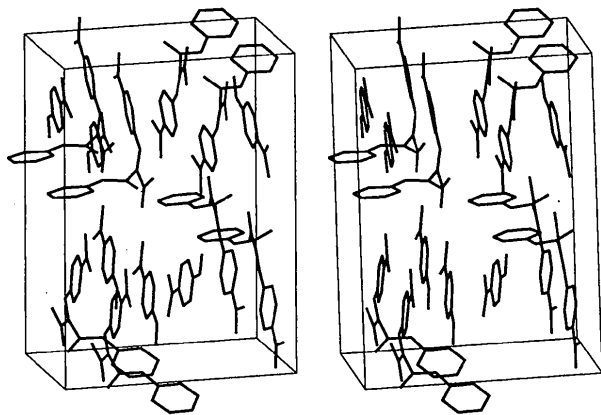

Fig. 1. Stereodrawing of the molecular packing. The origin is at the back lower right corner.

Comment

Synthesis of 2-[4-(dimethylamino)phenylimino]-3-oxo-N-phenylbutanamide (DPA) (Fig. 1) from acetanilide and N,N-dimethyl-4-nitroso-benzenamine (NDA) was undertaken as part of studies on charge-transfer complexes formed by 1-oxa-4-azabutadienes. The reaction mixture yielded the desired product but dark-green crystals, which had semiconductive properties, were also precipitated. On the basis of spectroscopic investigations, the structure of a polymeric quinhydrone-type charge-transfer complex of DPA and NDA was proposed (Moskal, Moskal & Milart, 1984). To verify this model we determined the crystal structure using X-ray diffraction methods.

DPA   NDA
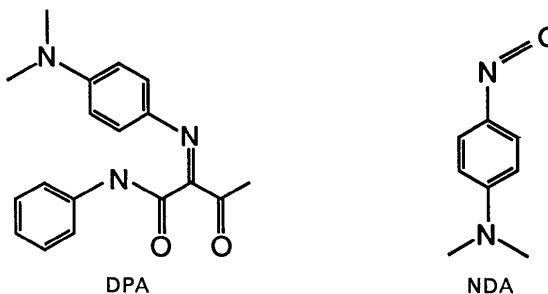
DPA (Fig. 2a) and NDA (Fig. 2b) molecules form double layers perpendicular to the [010] direction and related by a 2_1 axis. The mean separation between layers is about 3.5 Å. The DPA and NDA molecules are linked in pairs by a hydrogen bond between the anilide N atom of DPA and the nitroso O atom of NDA: N115···O209 = 2.813(2), H114···O209 = 1.98(2) Å and N115—H114···O209 = 162(2)°. As judged by the closest intermolecular contacts, which are 3.147(2) Å for O209—C102 and 3.339(2) Å for O209—C103, the nitroso group atoms are involved in π–π* interactions with the same DPA molecule. Other short intermolecular contacts observed between molecules in the same layer are C210—N207 = 3.193(2) and C211—O122 = 3.101(2) Å. Although the structure contains potential charge-transfer donors and acceptors stacked along [010], all other intermolecular contacts are longer than 3.4 Å, thus the interactions between layers should be classified as van der Waals contacts.

The distances in the NDA molecule show some distortion from the values expected in an aromatic ring and indicate a large contribution of the *para*-quinonoid structure. The observed pattern of bond lengths and angles in NDA is analogous to that observed in the structures of NDA.HCl.H2O (Drangfelt & Rømming, 1974) and the complexes CoCl(NDA)₂ (Sams & Doedens, 1979) and Cl₂Me₂(NDA)₂Sn (Matsubayashi & Nakatsu, 1982). Similar deformation is also observed in N,N-dimethylphenyl moiety of the DPA molecule, although to a lesser extent, presumably due to the formation of a double bond between N105 and C102 conjugated with
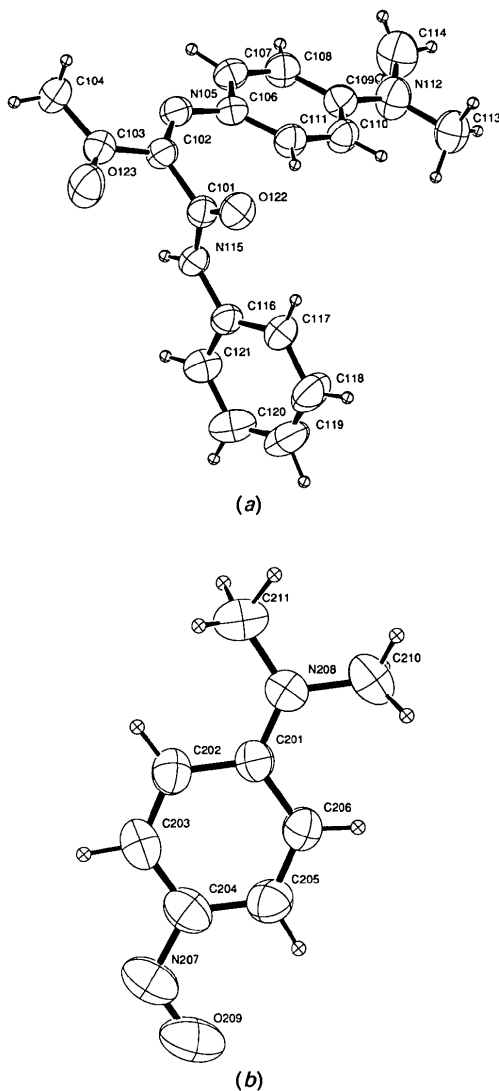
(a)

(b)

Fig. 2. View of (a) the DPA molecule and (b) the NDA molecule. H atoms are drawn as spheres of an arbitrary radius; only one set of H atoms is shown for the disordered methyl groups.

the acetyl group. Distances and angles within the acetanilide moiety of DPA are all as expected and are in good agreement with those observed in acetanilide (Wasserman, Ryan & Layne, 1985) and other N-aromatic amides (Kashino, Matsushita, Iwamoto, Yamaguchi & Haisa, 1986). The DPA molecule consists of two approximately planar portions twisted perpendicularly around the C101—C102 bond. This conformation is in agreement with the model proposed for α,β-dianils of α,β-diketobutyric acid anilides on the basis of spectroscopic investigations (Moskal, 1975). The least-squares plane through the C atoms of the phenyl ring of NDA forms dihedral angles of 5.81(5) and 83.55(6)° with the least-squares planes of the phenyl rings of DPA. The angle between the phenyl groups of DPA is 95.46(5)°.

Experimental

Crystal data

$C_{18}H_{19}N_3O_2.C_8H_{10}N_2O$	Cu $K\alpha$ radiation
$M_r = 459.55$	$\lambda = 1.54051$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 19.361$ (4) Å	$\theta = 9$–$30°$
$b = 13.942$ (3) Å	$\mu = 6.410$ mm^{-1}
$c = 9.054$ (3) Å	$T = 293$ K
$V = 2444$ (1) Å^3	Prism
$Z = 4$	$0.65 \times 0.45 \times 0.25$ mm
$D_x = 1.249$ Mg m^{-3}	Dark green

Data collection

Kuma KM-4 four-circle	$R_{int} = 0.011$
diffractometer	$\theta_{max} = 80.0°$
$\omega/2\theta$ scans	$h = -24 \rightarrow 24$
Absorption correction:	$k = -17 \rightarrow 0$
none	$l = 0 \rightarrow 11$
5918 measured reflections	2 standard reflections
5267 independent reflections	monitored every 50
5022 observed reflections	reflections
$[F > 3\sigma(F)]$	intensity variation: $\pm2\%$

Refinement

Refinement on F	$\Delta\rho_{min} = -0.242$ e Å^{-3}
Final $R = 0.035$	Extinction correction: empir-
$wR = 0.043$	ical (Sheldrick, 1976)
$S = 0.967$	Extinction coefficient:
5022 reflections	0.0023 (5)
484 parameters	Atomic scattering factors
All H-atom parameters re-	from International Tables
fined	for X-ray Crystallogra-
$w = 1/[\sigma^2(F)+0.003F^2]$	phy (1974, Vol. IV Table
$(\Delta/\sigma)_{max} = 0.028$	2.2B)
$\Delta\rho_{max} = 0.379$ e Å^{-3}	

Data collection: KM-4 software. Cell refinement: KM-4 software. Data reduction: KM-4 software. Program(s) used to solve structure: $SHELXS86$ (Sheldrick, 1985). Program(s) used to refine structure: $SHELX76$ (Sheldrick, 1976). Molecular graphics: $CHAIN$ (Sack, 1989), $MOLDRAW$ (Ugliengo, Borzani & Viterbo, 1988), $ORTEP$ (Johnson, 1965). Software used to prepare material for publication: $PARST88$ (Nardelli, 1983).

Least-squares refinement of H atoms showed that all methyl groups in both molecules suffer from disorder which could be resolved into two alternate sets of coordinates for the H atoms. Their positions were refined with fixed occupancies of 0.50. However, the poor geometry of the methyl groups indicates that this disorder could have, to some degree, rotational character.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C101	0.9141 (1)	0.3379 (1)	0.0872 (1)	0.0450 (5)
C102	0.8686 (1)	0.3627 (1)	0.2189 (1)	0.0457 (5)
C103	0.9052 (1)	0.3681 (1)	0.3642 (1)	0.0526 (6)
C104	0.8627 (1)	0.3841 (1)	0.5007 (2)	0.0636 (8)
N105	0.8030 (1)	0.3775 (1)	0.2157 (1)	0.0460 (4)
C106	0.7621 (1)	0.3749 (1)	0.0890 (1)	0.0440 (5)
C107	0.6908 (1)	0.3634 (1)	0.1111 (1)	0.0517 (6)

C108	0.6447 (1)	0.3589 (1)	−0.0047 (2)	0.0551 (6)
C109	0.6674 (1)	0.3690 (1)	−0.1516 (1)	0.0489 (5)
C110	0.7387 (1)	0.3844 (1)	−0.1735 (1)	0.0514 (5)
C111	0.7843 (1)	0.3872 (1)	−0.0574 (1)	0.0498 (5)
N112	0.6236 (1)	0.3655 (1)	−0.2690 (2)	0.0689 (7)
C113	0.6490 (1)	0.3745 (1)	−0.4193 (2)	0.0682 (8)
C114	0.5496 (1)	0.3673 (2)	−0.2515 (3)	0.0821 (12)
N115	0.9111 (1)	0.2435 (1)	0.0530 (1)	0.0478 (4)
C116	0.9418 (1)	0.1961 (1)	−0.0674 (1)	0.0475 (5)
C117	0.9715 (1)	0.2429 (1)	−0.1869 (1)	0.0611 (7)
C118	0.9985 (1)	0.1886 (2)	−0.3027 (2)	0.0792 (9)
C119	0.9971 (1)	0.0908 (2)	−0.2998 (2)	0.0806 (9)
C120	0.9680 (1)	0.0439 (1)	−0.1811 (2)	0.0756 (9)
C121	0.9400 (1)	0.0966 (1)	−0.0650 (2)	0.0597 (6)
O122	0.9474 (1)	0.3989 (1)	0.0225 (1)	0.0571 (4)
O123	0.9673 (1)	0.3572 (1)	0.3683 (1)	0.0775 (7)
C201	0.7964 (1)	−0.1173 (1)	0.2268 (1)	0.0482 (5)
C202	0.8365 (1)	−0.1144 (1)	0.0944 (1)	0.0583 (6)
C203	0.8053 (1)	−0.1214 (1)	−0.0397 (2)	0.0646 (7)
C204	0.7337 (1)	−0.1308 (1)	−0.0532 (2)	0.0624 (7)
C205	0.6933 (1)	−0.1342 (1)	0.0771 (2)	0.0620 (6)
C206	0.7234 (1)	−0.1282 (1)	0.2117 (2)	0.0577 (6)
N207	0.7082 (1)	−0.1364 (1)	−0.1938 (2)	0.0802 (8)
N208	0.8256 (1)	−0.1106 (1)	0.3596 (1)	0.0577 (5)
O209	0.6445 (1)	−0.1432 (1)	−0.2052 (2)	0.0945 (9)
C210	0.7847 (1)	−0.1185 (1)	0.4950 (2)	0.0680 (8)
C211	0.8990 (1)	−0.0962 (2)	0.3801 (2)	0.0832 (10)

Table 2. Geometric parameters (Å, °)

C101—C102	1.522 (2)	C116—C117	1.388 (2)
C101—N115	1.353 (2)	C116—C121	1.389 (2)
C101—O122	1.218 (2)	C117—C118	1.395 (2)
C102—C103	1.497 (2)	C118—C119	1.364 (3)
C102—N105	1.287 (2)	C119—C120	1.379 (3)
C103—C104	1.501 (2)	C120—C121	1.391 (2)
C103—O123	1.212 (2)	C201—C202	1.428 (2)
N105—C106	1.395 (2)	C201—C206	1.428 (2)
C106—C107	1.404 (2)	C201—N208	1.331 (2)
C106—C111	1.404 (2)	C202—C203	1.359 (2)
C107—C108	1.378 (2)	C203—C204	1.399 (2)
C108—C109	1.408 (2)	C204—C205	1.416 (2)
C109—C110	1.411 (2)	C204—N207	1.367 (2)
C109—N112	1.361 (2)	C205—C206	1.354 (2)
C110—C111	1.372 (2)	N207—O209	1.243 (3)
N112—C113	1.453 (2)	N208—C210	1.462 (2)
N112—C114	1.441 (2)	N208—C211	1.449 (2)
N115—C116	1.406 (2)		

N115—C101—O122	126.2 (1)	C101—N115—C116	128.1 (1)
C102—C101—O122	121.7 (1)	N115—C116—C121	116.6 (1)
C102—C101—N115	112.1 (1)	N115—C116—C117	123.9 (1)
C101—C102—N105	126.2 (1)	C117—C116—C121	119.5 (1)
C101—C102—C103	115.2 (1)	C116—C117—C118	119.1 (2)
C103—C102—N105	118.7 (1)	C117—C118—C119	121.4 (2)
C102—C103—O123	119.4 (1)	C118—C119—C120	119.8 (2)
C102—C103—C104	118.1 (1)	C119—C120—C121	119.8 (2)
C104—C103—O123	122.5 (2)	C116—C121—C120	120.4 (2)
C102—N105—C106	125.0 (1)	C206—C201—N208	120.9 (1)
N105—C106—C111	126.9 (1)	C202—C201—N208	121.8 (1)
N105—C106—C107	116.3 (1)	C202—C201—C206	117.4 (1)
C107—C106—C111	116.7 (1)	C201—C202—C203	120.5 (1)
C106—C107—C108	122.2 (1)	C202—C203—C204	121.7 (2)
C107—C108—C109	120.8 (1)	C203—C204—N207	116.4 (2)
C108—C109—N112	122.7 (1)	C203—C204—C205	118.5 (2)
C108—C109—C110	116.9 (1)	C205—C204—N207	125.1 (2)
C110—C109—N112	120.4 (1)	C204—C205—C206	120.7 (1)
C109—C110—C111	121.7 (1)	C201—C206—C205	121.3 (1)
C106—C111—C110	121.6 (1)	C204—N207—O209	116.1 (2)
C109—N112—C114	122.2 (2)	C201—N208—C211	122.8 (2)
C109—N112—C113	121.2 (1)	C201—N208—C210	121.5 (1)
C113—N112—C114	116.0 (2)	C210—N208—C211	115.7 (2)

C102—C101—N115—C116	174.8 (1)
N115—C101—C102—N105	−81.3 (2)
O122—C101—C102—C103	−83.5 (2)
C101—C102—N105—C106	−1.2 (2)
N105—C102—C103—O123	−177.8 (1)
C102—N105—C106—C107	161.0 (1)

C108—C109—N112—C114	10.7 (3)
C110—C109—N112—C113	1.9 (2)
C101—N115—C116—C121	170.2 (1)
C206—C201—N208—C210	2.9 (2)
C202—C201—N208—C211	2.4 (2)
C205—C204—N207—O209	1.4 (3)

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1,4-Bis(4-chlorobenzoyl)-2,3,5,6-tetramethylbenzene

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Abstract

In $Cl—C_6H_4—CO—C_6Me_4—CO—C_6H_4—Cl$, steric hindrance due to four methyl substituents in the central ring of the title compound causes the two p-chlorobenzoyl