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Strong overcrowding in dimethyl 2-(dimethylamino)terephthalate

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The molecular structure of the title compound, $C_{12}H_{15}NO_4$, has several features related to steric hindrance due to the ester and dimethylamine groups being located *ortho* with respect to one another. In particular, the carbonyl group of the ester is not coplanar with the ring, the amine N atom is in a pyramidal arrangement [the N atom is 0.2161 (12) Å from the three C atoms to which it is bonded] and the C atom of the adjacent ester group lies 0.3784 (14) Å out of the plane of the aromatic ring. The deformations found in the X-ray structure have been confirmed by *ab initio* quantum mechanical calculations.

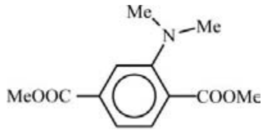
Comment

The title compound, (I), has been prepared as an electron-rich intermediate in the synthesis of new polymeric materials for electronics and photonics. In many of these systems, π conjugation between electron-rich and electron-poor moieties along the polymer chain is required (Dhanabalan *et al.*, 2001).

The determination of the X-ray structure of (I) (Fig. 1) was undertaken on the basis of the presumed effects of steric overcrowding due to the location of the ester and dimethylamine groups *ortho* to one another; this configuration could affect the planarity of the molecule and hence the π conjugation and performance of the derived compounds.

In terephthalic or benzoic acid derivatives, the carbonyl group is generally found to be coplanar with the benzene ring (Centore *et al.*, 1991; Centore & Tuzi, 1998). Deviations from coplanarity are observed as a result of steric overcrowding, *e.g.* for 2,6-disubstituted benzoic acids (Anca *et al.*, 1967; Florencio & Smith, 1970).

Of the two carbonyl groups of (I), C9/O3 is essentially coplanar with the ring, as expected, while C2/O1, located *ortho* to the dimethylamine group, is not. The torsion of the carbonyl group does not fully relax the steric overcrowding, because of the contact between atom O1 and one of the H atoms bonded to atom C11. The dimethylamine group is also involved in the pattern of deformations.



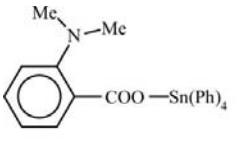
(I)

In the absence of steric overcrowding, *N*,*N*-dialkylamine groups are often found to be essentially coplanar with benzene rings, and the geometry about the N atom is trigonal planar, the sp^2-hybridization favouring interaction of the lone pair with the π electrons of the ring (Centore *et al.*, 1997, 2002; Centore & Tuzi, 2001; Castaldo *et al.*, 2002). In (I), the N atom is in a pyramidal arrangement [the sum of the valence angles around N1 is 353.3 (1)°]. Moreover, the disposition of the dimethylamine group is not symmetric with respect to the benzene ring. In fact, the methyl group not involved in the close contact (C12) is essentially coplanar with the ring [0.133 (3) Å below the mean plane], while the other is not [0.874 (3) Å below the mean plane]. On the other hand, atom O1 lies 1.176 (3) Å above the mean plane of the ring.

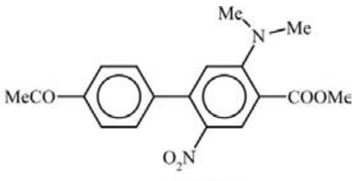
An additional piece of structural evidence probably still related to the steric overcrowding is the out-of-plane deformation of carbonyl atom C2. Actually, the benzene ring is planar within 0.039 (1) Å, and atom C2 lies 0.378 (2) Å above the mean plane of the ring. It is worth noting that the same type of deformation is not observed for atom N1, probably because of the π–π interaction between the N atom and the ring.

In summary, all of the deformations described above drive the nonbonded distance O1$\cdots$C11 to 2.950 (2) Å.

We have searched the Cambridge Structural Database (Version 5.29; Allen, 2002) for compounds having an *N*,*N*-dimethylamine and a COO group *ortho* to one another. Out of the four hits found (refcodes CUNJEA, DOZDAX, ISOGOM and XERCOM), two are significant in this context (see Table 2). In one case (refcode CUNJEA; Swisher *et al.*, 1984) the pattern of deformations is very similar to the present one. In the other (refcode ISOGOM; Davies *et al.*, 2004), the pattern is different. In fact, the N atom has a trigonal planar geometry, with the plane twisted with respect to the benzene ring (by about 20°); a higher twist of the carbonyl group is observed and the carbonyl C atom is essentially coplanar with the ring. The different pattern observed in ISOGOM is probably due to the nitro group being in the *para* position with respect to the dimethylamine group (push–pull effect).



CUNJEA



ISOGOM

In view of the different deformations found in the X-ray structures, we have performed a theoretical quantum

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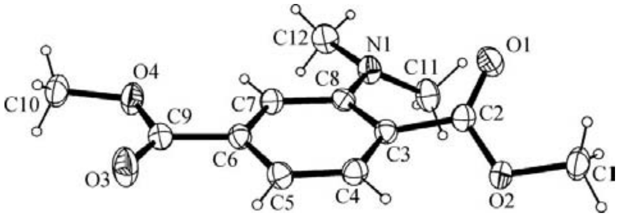

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Only one position is shown for H atoms of disordered methyl groups.

mechanical calculation of the gas phase molecular structure of (I) in order to verify the equilibrium geometry of the isolated molecule. The calculations were performed using density functional theory, using the hybrid B3LYP exchange-correlation functional and the standard 6–31++G** basis set. All computations were performed using the *GAUSSIAN03* package (Frisch *et al.*, 2003).

There is a good agreement between the experimental and the computed molecular geometry (see Table 3); the bond lengths do not differ by more than 0.016 Å and the bond angles differ by a maximum of 1.6°. The three main structural effects related to the steric overcrowding, *i.e.* the torsion angle of the carbonyl group around C2—C3, the deformation of the dimethylamine group and the out-of-plane displacement of atom C2, are found also in the calculated geometry.

The UV–Vis characterization of (I) in chloroform solution shows the HOMO–LUMO band centred at λ_{max} = 350 nm, with a tail in the visible region, responsible for the yellow colour of (I). By exciting the compound at 350 nm, emission at 425 nm is observed (blue fluorescence). The measured quantum yield is 0.091.

Experimental

2-Aminoterephthalic acid (10 g, 55 mmol), methyl iodide (62.5 g, 440 mmol), potassium carbonate (30.4 g) and *N*,*N*-dimethylformamide (58 ml) were stirred at room temperature for 4 d in a round-bottomed flask equipped with a condenser connected to air through a $CaCl_2$ trap. The inorganic solid was filtered off and the solution was poured into water (200 ml) at 273–278 K with stirring. Within minutes, a pasty solid formed. The solution was filtered, the solid obtained dissolved in chloroform and anhydrified over sodium sulfate, and the excess chloroform distilled off. A yellow oil of (I) was finally obtained, which crystallized after several days (m.p. 322 K). Crystals of (I) suitable for structure determination were obtained by slow evaporation of a dichloromethane solution at room temperature. ^{1}H NMR (200 MHz, 298 K, $CDCl_3$): δ 2.89 (*s*, 6H, NCH_3), 3.91 (*s*, 6H, OCH_3), 7.45 (*d*, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz, Ph), 7.598 (*s*, 1H, Ph), 7.66 (*d*, 1H, J_1 = 8.0 Hz, Ph).

Crystal data

$C_{12}H_{15}NO_4$
M_r = 237.25
Triclinic, $P\bar{1}$
a = 7.7120 (7) Å
b = 7.9190 (8) Å
c = 9.989 (3) Å
α = 74.624 (14)°
β = 82.576 (16)°
γ = 85.663 (9)°
V = 582.7 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 173 (2) K
0.38 × 0.33 × 0.28 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker–Nonius, 2002)
T_{min} = 0.952, T_{max} = 0.972
8647 measured reflections
2622 independent reflections
1977 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
S = 1.05
2622 reflections
158 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.2095 (17)	C2—C3	1.4971 (18)
O3—C9	1.2035 (17)	C6—C9	1.5026 (18)
N1—C8	1.3819 (17)		
C8—N1—C11	120.81 (12)	C8—C3—C2	122.65 (11)
C8—N1—C12	118.93 (11)	N1—C8—C7	120.39 (11)
C11—N1—C12	113.52 (11)	N1—C8—C3	122.74 (11)
C4—C3—C8	119.69 (11)	C7—C8—C3	116.87 (12)
C4—C3—C2	116.99 (11)		
O1—C2—C3—C8	36.5 (2)	C11—N1—C8—C3	33.88 (19)
C4—C5—C6—C9	−176.17 (12)	C2—C3—C8—C7	−163.11 (12)
C12—N1—C8—C7	3.25 (19)	C5—C6—C9—O3	1.0 (2)

Table 2
Comparative structural data (Å, °) for (I), CUNJEA and ISOGOM.

	(I)[a]	CUNJEA[b]	ISOGOM[c]
O1—C2—C3—C8	36.5 (2)	43.8	−61.5
C2—C3—C8—C7	−163.11 (12)	166.7	−175.7
C11—N1—C8—C3	33.88 (19)	44.0	−21.7
C12—N1—C8—C7	3.25 (19)	6.5	−14.9
τ_{N1}[d]	353.3 (1)	349.2	359.5
O1···C11	2.950 (2)	3.06	3.01

(*a*) This work; (*b*) Swisher *et al.* (1984); (*c*) Davies *et al.* (2004); (*d*) τ_{N1} is the sum of the valence angles at N1.

Table 3
Selected geometric parameters (Å, °) for the calculated equilibrium geometry of (I).

O1—C2	1.219	C2—C3	1.489
O3—C9	1.217	C6—C9	1.494
N1—C8	1.383		
C8—N1—C11	122.19	C8—C3—C2	122.45
C8—N1—C12	120.37	N1—C8—C7	119.59
C11—N1—C12	114.54	N1—C8—C3	123.10
C4—C3—C8	119.44	C7—C8—C3	117.30
C4—C3—C2	117.54		
O1—C2—C3—C8	23.5	C11—N1—C8—C3	38.1
C4—C5—C6—C9	−179	C2—C3—C8—C7	−165.6
C12—N1—C8—C7	18.4	C5—C6—C9—O3	−0.5

H atoms were positioned stereochemically and constrained using a riding model, with U_{iso}(H) values set at 1.2U_{eq} of the carrier atom for ring H atoms or at 1.5U_{eq} of the carrier atom for methyl H atoms. For H atoms of methyl groups, the conformation was defined on the basis of difference maps. The H atoms of the two ester methyl groups and the methylamine group (C11) are disordered over two sites rotated by 60° with respect to each other.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3150). Services for accessing these data are described at the back of the journal.

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