

H(7n) of a molecule centered at x,y,z hydrogen bonds to O(8) of a molecule centered at $1+x,y,z$. This interaction [$H\cdots O$, 1.71 (8) Å, $N\cdots O$, 2.785 (8) Å; $N-H\cdots O$, 160.4°] is shown by a dashed line in Fig. 2. Though the molecule could form a six-membered ring [C(1), C(6), N(6), O(6b), H(7n), N(7)] by hydrogen bonding intramolecularly, a close intermolecular association is adopted in this crystal form. In fact, H(7n) points 'above' the average molecular plane whereas O(6b) points 'below' the molecular plane, giving an $H(7n)\cdots O(6b)$ intramolecular distance of 2.47 Å.

The N(nitro)—C distances are all 1.48 (1) Å and are significantly longer than the N(7)—C(1) (amide—phenyl ring) linkage [1.41 (1) Å], consistent with previous observations that C—NO₂ distances tend to be longer than C—N(amine) bonds to aromatic rings (Ammon & Prasad, 1985; Cady & Larson, 1965).

The nitro groups display a range of torsion angles relative to the aromatic ring. For the N(2), N(4) and N(6) nitro groups, the signed twist angles [averaged torsion angles defined by Winkler & Dunitz (1971)] are +44.2 (5), -16.5 (5) and +37.2 (5)°, respectively. Though the torsion angle of N(4) is small enough to consider a cross-ring resonance with the amide nitrogen, the twist angle of the amide

moiety relative to the phenyl ring is +47.8°, making its resonance with the ring unlikely. The similarity of the ring—nitro group distances also argues against any appreciable resonance effects. Indeed, resonance of the nitro group of nitrobenzene, which is coplanar with the benzene ring, has recently been challenged (Politzer, Lane, Jayasuriya & Domelsmith, 1987).

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Structure of Ethyl (3-Methyl-2,4,6-trinitrophenyl)carbamate Dimethyl Sulfoxide Solvate

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Abstract. C₁₀H₁₀N₄O₈·C₂H₆OS, $M_r = 392.38$, triclinic, $P\bar{1}$, $a = 8.516$ (2), $b = 9.688$ (2), $c = 11.895$ (3) Å, $\alpha = 73.43$ (2), $\beta = 80.78$ (2), $\gamma = 72.07$ (2)°, $V = 892.1$ (4) Å³, $Z = 2$, $D_x = 1.461$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.224$ mm⁻¹, $F(000) = 408$, $T = 275$ K, final $R = 0.051$, $wR = 0.050$ for 1821 independent reflections. The title compound is hydrogen bonded through the amide hydrogen to the dimethyl sulfoxide (DMSO) molecule. The molecule is virtually identical to ethyl (2,4,6-trinitrophenyl)carbamate except for (a) the intermolecular hydrogen bonding and (b) the methyl

group of the title compound which significantly distorts the intra-annular angle of the aromatic carbon to which it is bonded.

Introduction. Polynitroaromatic compounds are important as high-energy materials (propellants and explosives). They have also received attention since the nitro groups can cause significant distortions of aromatic rings from idealized structures. Though chemically very similar to the previously reported (Dudis & Gilardi, 1990) ethyl (2,4,6-trinitrophenyl)carbamate (II), the title compound (I) has a

much more distorted ring than (II). A comparison of similar distances and angles in these molecules shows similar sections of them to be statistically indistinguishable, indicating that the differences probably arise from replacement of H in (II) by methyl in (I), rather than from crystal packing forces.

Experimental. A clear colorless $0.60 \times 0.18 \times 0.12$ mm data crystal was grown from DMSO from material provided by Dr Paul Bolduc of Eglin Air Force Base. Automated Nicolet R3m diffractometer with incident beam monochromator. 25 centered reflections within $21 \leq 2\theta \leq 25^\circ$ used for determining lattice parameters. $[\sin(\theta)/\lambda]_{\max} = 0.54 \text{ \AA}^{-1}$, range of hkl : $0 \leq h \leq 9$, $-9 \leq k \leq 9$, $-13 \leq l \leq 12$. Standards 220, 020, 003, monitored every 60 reflections with 3% random variation over data collection, $\theta-2\theta$ mode, θ scan width 0.8° , θ scan rate $15^\circ \text{ min}^{-1}$; 2619 reflections measured, 2347 unique, $R_{\text{int}} = 0.007$, 1821 observed with $F_o > 3\sigma(|F_o|)$. Data corrected for Lorentz, polarization and absorption effects (numerical absorption correction based on crystal faces); 0.862, 0.970 min., max. transmission factors. Structure solved by direct methods. Least-squares refinement using *SHELXTL80* (Sheldrick 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, $g = 0.00025$. Secondary extinction parameter $p = 0.0073$ (8) in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$. 273 parameters refined: atom coordinates, anisotropic thermal parameters for all non-H atoms, H atoms included using riding model (coordinate shifts of C applied to attached H atoms), C—H = 0.96 \AA , H—C—H = 109.5° , $U(\text{H}) = 1.1 \times U_{\text{eq}}(\text{C})$, except for H(3a1), H(3a2), H(3a3), H(1N), H(1b1), H(1b2), and H(5) (see Fig. 1) whose positions and isotropic thermal factors were refined. $(\Delta/\sigma)_{\max} = 0.01$, $R = 0.051$, $wR = 0.050$, $S = 1.41$. (For all 2347 unique data, $R = 0.067$, $wR = 0.052$.)

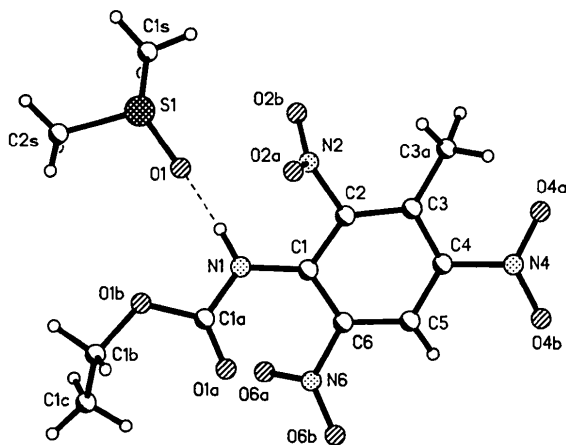


Fig. 1. Perspective drawing of the title compound showing numbering scheme and interaction with DMSO molecule.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	7209 (5)	5139 (4)	5805 (3)	34 (2)
N(1)	6739 (5)	4385 (4)	6935 (3)	40 (2)
C(1a)	7514 (5)	2926 (5)	7418 (3)	41 (2)
O(1a)	8736 (3)	2175 (3)	6996 (2)	48 (1)
O(1b)	6735 (4)	2475 (3)	8475 (2)	54 (1)
C(1b)	7356 (8)	917 (5)	9095 (5)	61 (3)
C(1c)	6737 (8)	-73 (6)	8646 (5)	89 (3)
C(2)	7311 (5)	6598 (4)	5604 (3)	33 (2)
N(2)	7079 (5)	7174 (4)	6667 (3)	45 (2)
O(2a)	8243 (5)	6753 (4)	7265 (3)	70 (2)
O(2b)	5747 (5)	8027 (4)	6866 (3)	78 (2)
C(3)	7630 (5)	7543 (4)	4525 (3)	37 (2)
C(3a)	7703 (7)	9095 (5)	4429 (5)	52 (2)
C(4)	7947 (5)	6866 (5)	3587 (3)	40 (2)
N(4)	8239 (5)	7715 (5)	2358 (3)	56 (2)
O(4a)	7609 (5)	9069 (4)	2099 (3)	76 (2)
O(4b)	9065 (5)	6995 (4)	1656 (3)	74 (2)
C(5)	7981 (5)	5391 (5)	3725 (4)	44 (2)
C(6)	7568 (5)	4558 (4)	4821 (3)	38 (2)
N(6)	7423 (5)	3070 (4)	4861 (3)	47 (2)
O(6a)	6191 (4)	2730 (3)	5403 (3)	63 (2)
O(6b)	8521 (4)	2286 (3)	4328 (3)	67 (2)
S(1)	3156 (2)	6270 (1)	8951 (1)	55 (1)
O(1)	3714 (4)	5667 (3)	7886 (3)	65 (2)
C(1s)	1216 (6)	7591 (6)	8660 (5)	76 (3)
C(2s)	2443 (7)	4884 (6)	10034 (5)	82 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)—N(1)	1.396 (4)	C(1)—C(2)	1.392 (6)
C(1)—C(6)	1.391 (6)	N(1)—C(1a)	1.359 (5)
C(1a)—O(1a)	1.200 (5)	C(1a)—O(1b)	1.345 (5)
O(1b)—C(1b)	1.450 (5)	C(1b)—C(1c)	1.475 (10)
C(2)—N(2)	1.484 (6)	C(2)—C(3)	1.389 (5)
N(2)—O(2a)	1.211 (6)	N(2)—O(2b)	1.214 (5)
C(3)—C(3a)	1.495 (7)	C(3)—C(4)	1.400 (6)
C(4)—N(4)	1.483 (5)	C(4)—C(5)	1.383 (7)
N(4)—O(4a)	1.221 (6)	N(4)—O(4b)	1.233 (5)
C(5)—C(6)	1.380 (5)	C(6)—N(6)	1.471 (6)
N(6)—O(6a)	1.224 (5)	N(6)—O(6b)	1.225 (5)
S(1)—O(1)	1.494 (4)	S(1)—C(1s)	1.766 (5)
S(1)—C(2s)	1.759 (6)		
N(1)—C(1)—C(2)	119.4 (4)	N(1)—C(1)—C(6)	125.1 (4)
C(2)—C(1)—C(6)	115.5 (3)	C(1)—N(1)—C(1a)	122.2 (3)
N(1)—C(1a)—O(1a)	125.7 (4)	N(1)—C(1a)—O(1b)	109.0 (3)
O(1a)—C(1a)—O(1b)	125.2 (3)	C(1a)—O(1b)—C(1b)	116.5 (3)
O(1b)—C(1b)—C(1c)	111.5 (5)	C(1)—C(2)—N(2)	115.7 (3)
C(1)—C(2)—C(3)	126.8 (4)	N(2)—C(2)—C(3)	117.5 (4)
C(2)—N(2)—O(2a)	116.9 (3)	C(2)—N(2)—O(2b)	117.8 (4)
O(2a)—N(2)—O(2b)	125.3 (4)	C(2)—C(3)—C(3a)	121.5 (4)
C(2)—C(3)—C(4)	113.4 (4)	C(3a)—C(3)—C(4)	125.1 (4)
C(3)—C(4)—N(4)	121.4 (4)	C(3)—C(4)—C(5)	123.3 (3)
N(4)—C(4)—C(5)	115.3 (4)	C(4)—N(4)—O(4a)	118.1 (4)
C(4)—N(4)—O(4b)	117.4 (4)	O(4a)—N(4)—O(4b)	124.4 (3)
C(4)—C(5)—C(6)	119.3 (4)	C(1)—C(6)—C(5)	121.6 (4)
C(1)—C(6)—N(6)	122.6 (3)	C(5)—C(6)—N(6)	115.7 (4)
C(6)—N(6)—O(6a)	117.2 (3)	C(6)—N(6)—O(6b)	117.5 (4)
O(6a)—N(6)—O(6b)	125.3 (4)	O(1)—S(1)—C(1s)	105.5 (2)
O(1)—S(1)—C(2s)	106.2 (3)	C(1s)—S(1)—C(2s)	97.8 (2)

Final difference Fourier excursions 0.26 and -0.20 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. A perspective drawing of (I) indicating the numbering scheme is shown in Fig. 1. Non-H

atomic coordinates are given in Table 1* while bond lengths and bond angles are given in Table 2. All bond lengths and angles are within reasonable ranges. An N—H...O hydrogen bond, with H...O = 1.79 (4) and N...O = 2.711 (5) Å, joins the amide hydrogen to the DMSO oxygen. The closest non-bonded intermolecular contact is 2.43 (5) Å from the DMSO O atom O1, to a phenyl H atom, H5, in the inversion-related molecule at 1 - x, 1 - y, 1 - z.

The title compound and DMSO solvate exist as discrete, hydrogen-bonded dimers. This contrasts with the crystal structure of (II) in which molecules of (II) hydrogen-bond to form infinite chains, using the amide hydrogen of one molecule and the amide (carbonyl) oxygen of the next. However, this introduces very few differences between (I) and (II). All the comparable bond distances in the amide moieties are statistically identical. Thus, as far as internal amide geometry is concerned, it appears to make relatively little difference whether it is hydrogen bonded to a DMSO molecule or to another carbamate molecule. The twist angles of the amide groups relative to the phenyl rings are 43.5 (4)° in (I) and 47.8 (8)° in (II). [Twist angles, which have enantiomorph-sensitive signs, were defined by Wink-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52471 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

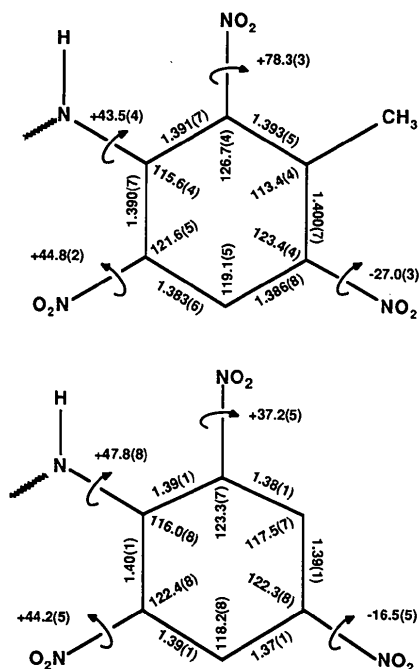


Fig. 2. Comparison of internal phenyl bond distances and angles and the substituent twist angles for (I) and (II).

ler & Dunitz (1971) for convenience in analyzing and discussing linked semiplanar moieties. We have modified their definition to include experimental uncertainties as weighting factors. Here, twist angles are calculated according to $T = (w_1\tau_1 + w_2\tau_2 + w_3\tau_3 + w_4\tau_4) \bmod 2\pi / (w_1 + w_2 + w_3 + w_4)$, where the τ_i 's are the four experimental torsions about the *exo*-phenyl substituent bond and the w_i 's are their individual weights ($w_i = 1/\sigma_i^2$).

Fig. 2 makes a detailed comparison of the internal bond distances and angles in the benzene rings of (I) and (II), and the twist angles of the nitro and amide substituents. The rings of the respective molecules have comparable orientations relative to the amide hydrogens so valid comparisons can be made. Chemically similar parameters for each ring are indistinguishable (well under 2σ) except for the internal angle of the methyl-substituted carbon of (I), the internal angle of the phenyl carbon between the methyl-substituted position and the amide function, and the twist angles of the nitro groups adjacent to the methyl-substituted position. The internal phenyl angle at the methyl substituted carbon [113.4 (4)°] differs by 5.9σ from the corresponding angle in (II) [117.5 (7)°]. The internal angle of the adjacent carbon (between the amide-substituted and methyl-substituted phenyl carbons) is enlarged to 126.7 (4)° compared with 123.3 (7)° in (II) (a 4.9σ difference). This is consistent with previous observations (Domenicano, Vacigo & Coulson, 1975) that strongly electron-withdrawing groups cause increases in this internal angle whereas electron-releasing groups tend to cause a decrease. This is borne out in the substitution of methyl for hydrogen [(I) vs. (II)]. Given the similarities in the other parts of the molecules, and the negligible effect of the nearest (hydrogen-bonded) neighboring molecule, it is reasonable to conclude that these differences are due to electronic and/or intramolecular steric effects rather than crystal packing forces.

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