Structure of 1-(4-Nitrobenzoyloxy)-4,5-dimethyl-1,2,3-triazole

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Abstract. 4,5-Dimethyl-1,2,3-triazol-1-yl *p*-nitro-benzoate, $C_{11}H_{10}N_4O_4$, $M_r = 262.22$, orthorhombic, $P2_12_12_1$, $a = 5.945$ (1), $b = 10.941$ (2), $c = 18.277$ (4) Å, $V = 1188.8$ (8) Å^3, $Z = 4$, $D_m = 1.45$, $D_x = 1.47$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.07$ cm^{-1}, $F(000) = 544$, $T = 298$ K, final $R = 0.0349$, $wR = 0.0520$ for 1165 observed reflections. The crystal and molecular structure of the title compound have been determined and compared to the reported crystal structures of the related *p*-chloro derivative and *N*-benzoyloxybenzotriazole. In all three compounds, the two aromatic rings are nearly orthogonal. Semi-empirical (*AM*1) molecular-orbital calculations exhibit energy maxima when the triazole ring and carboxylate group are coplanar. Energy-minimized (*AM*1) and observed (X-ray) geometries for all three compounds are compared.

Introduction. The title compound (1) (NBODT) was prepared by lead tetraacetate oxidation of the corresponding hydroxyiminoaroylhydrazone of biacetyl in a fashion similar to that used to prepare related compounds in this series with different substituents on the phenyl ring (H, CH_3, Cl, CH_3O and NO_2) (Theocharis, Maroulis, Hadjiantoniou-Maroulis & Alexandrou, 1989). Analysis based on ^{1}H and ^{13}C NMR spectra did not allow unambiguous structural assignment of this or other members of the series, since the facile rearrangement of relate⁴ ₐcyloxybenzotriazoles has been well documented (Nagaragan, Wilson & Rinehart, 1985). Previous reports describing the structures of 1-(4-

chlorobenzoyloxy)-4,5-dimethyl-1,2,3-triazole [(2), CBODT] (Kavounis, Bozopoulos, Cheer & Rentzeperis, 1988) and 1-benzoyloxybenzotriazole [(3), BBT] (McCarthy, Hegarty & Hathaway, 1977) indicate that both of these substances exist in the solid state as *N*-benzoyloxy esters. In both of these substances, as well as the title compound, the triazole and benzoyloxy groups are observed to be nearly orthogonal. In order to determine whether this conformational bias was the result of packing effects or represented an intrinsic property of *N*-benzoyloxy-triazoles, a semi-empirical (*AM*1) (Dewar, Zoebisch, Healey & Stewart, 1985) molecular-orbital study was undertaken. Calculated heats of formation of rotamers of NBODT about the N—O bond reveal two maxima when the triazole and benzoyloxy groups are coplanar. The calculations also predict energy minima when these groups are nearly orthogonal, at geometries very similar to those observed in the crystal structures. A graph of the NBODT N(2)—N(1)—O(1)—C(3) torsion angle against *AM*1 calculated heat of formation is shown in Fig. 1.
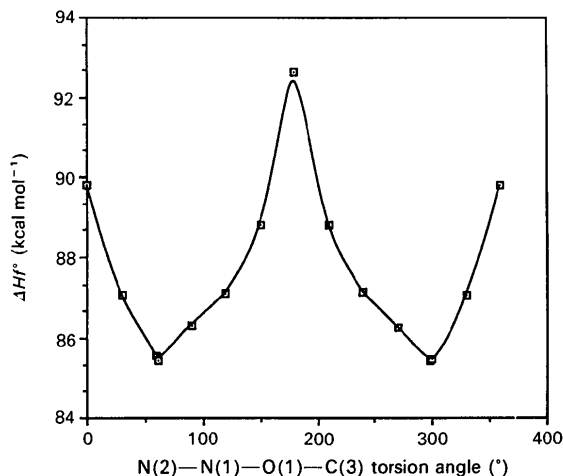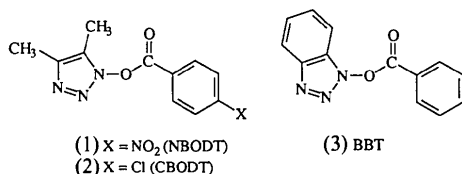
(1) X = NO₂ (NBODT)
(2) X = Cl (CBODT)

(3) BBT

Fig. 1. *AM*1-calculated heat of formation for various rotamers of NBODT about the N(2)—N(1)—O(1)—C(3) torsion angle (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹).

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$)

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

	x	y	z	U_{eq}
C(1)	−2521 (3)	6356 (2)	6001 (1)	41 (1)
C(2)	−2641 (3)	5952 (2)	5294 (1)	39 (1)
C(3)	−896 (3)	3621 (2)	4478 (1)	42 (1)
C(4)	253 (3)	2963 (2)	3881 (1)	36 (1)
C(5)	−708 (3)	1861 (2)	3660 (1)	43 (1)
C(6)	331 (3)	1166 (2)	3133 (1)	44 (1)
C(7)	2331 (3)	1565 (2)	2845 (1)	39 (1)
C(8)	3309 (4)	2668 (2)	3039 (1)	44 (1)
C(9)	2234 (3)	3373 (2)	3562 (1)	44 (1)
C(10)	−4174 (4)	7112 (2)	6418 (1)	57 (1)
C(11)	−4343 (4)	6098 (3)	4709 (1)	61 (1)
N(1)	−701 (3)	5327 (1)	5225 (1)	41 (1)
N(2)	573 (3)	5315 (2)	5824 (1)	53 (1)
N(3)	−566 (3)	5964 (2)	6306 (1)	50 (1)
N(4)	3484 (3)	799 (2)	2302 (1)	48 (1)
O(1)	121 (2)	4757 (1)	4605 (1)	46 (1)
O(2)	−2470 (3)	3285 (1)	4822 (1)	64 (1)
O(3)	.2434 (3)	−34 (2)	2021 (1)	70 (1)
O(4)	5433 (3)	1019 (2)	2163 (1)	69 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)—C(2)	1.368 (3)	C(1)—C(10)	1.493 (3)	
C(1)—N(3)	1.358 (3)	C(2)—C(11)	1.480 (3)	
C(2)—N(1)	1.347 (2)	C(3)—C(4)	1.475 (3)	
C(3)—O(1)	1.401 (2)	C(3)—O(2)	1.186 (3)	
C(4)—C(5)	1.393 (3)	C(4)—C(9)	1.389 (3)	
C(5)—C(6)	1.374 (3)	C(6)—C(7)	1.372 (3)	
C(7)—C(8)	1.385 (3)	C(7)—N(4)	1.470 (2)	
C(8)—C(9)	1.384 (3)	N(1)—N(2)	1.330 (2)	
N(1)—O(1)	1.384 (2)	N(2)—N(3)	1.318 (3)	
N(4)—O(3)	1.217 (2)	N(4)—O(4)	1.211 (3)	
C(2)—C(1)—C(10)	128.8 (2)	C(2)—C(1)—N(3)	109.2 (2)	
C(10)—C(1)—N(3)	122.0 (2)	C(1)—C(2)—C(11)	133.1 (2)	
C(1)—C(2)—N(1)	102.0 (2)	C(11)—C(2)—N(1)	124.9 (2)	
C(4)—C(3)—O(1)	110.9 (2)	C(4)—C(3)—O(2)	127.3 (2)	
O(1)—C(3)—O(2)	121.8 (2)	C(3)—C(4)—C(5)	116.5 (2)	
C(3)—C(4)—C(9)	123.1 (2)	C(5)—C(4)—C(9)	120.4 (2)	
C(4)—C(5)—C(6)	119.9 (2)	C(5)—C(6)—C(7)	118.8 (2)	
C(6)—C(7)—C(8)	122.9 (2)	C(6)—C(7)—N(4)	118.8 (2)	
C(8)—C(7)—N(4)	118.3 (2)	C(7)—C(8)—C(9)	117.9 (2)	
C(4)—C(9)—C(8)	120.1 (2)	C(2)—N(1)—N(2)	114.6 (2)	
C(2)—N(1)—O(1)	127.4 (2)	N(2)—N(1)—O(1)	117.9 (2)	
N(1)—N(2)—N(3)	104.6 (2)	C(1)—N(3)—N(2)	109.6 (2)	
C(7)—N(4)—O(3)	118.2 (2)	C(7)—N(4)—O(4)	118.3 (2)	
O(3)—N(4)—O(4)	123.4 (2)	C(3)—O(1)—N(1)	112.6 (1)	

Experimental. The data crystal was a pale-yellow blunt needle, measuring $0.25 \times 0.30 \times 0.45$ mm. D_m by flotation in hexane/CCl_4. Data were collected on a computer-controlled Nicolet $R3m/E$ autodiffractometer, using graphite-monochromated Mo $K\alpha$ radiation, variable speed (4.88–29.30° min^{-1}) $\theta/2\theta$ scans, with a scan range of 1.0° and backgrounds measured at 0.25° on either side of the scan range. Lattice parameters were calculated from 25 carefully centered reflections between 20.0 and 36.0° 2θ. 1285 reflections between 3.5 and 45° 2θ (with index ranges $0 \le h \le 7$, $0 \le k \le 13$, $0 \le l \le 21$) were collected, of which 1239 were unique and 1165 had $I_o > 4\sigma(I_o)$ and were considered observed. There was no deterioration of three standard reflections (148, 174 and 338, which varied between 0.9858 and 1.0103) measured every 100 reflections. The data were corrected for Lorentz and polarization effects; a profile analysis correction was applied but no absorption corrections were made ($\mu = 1.07$ cm^{-1}). The structure was solved by direct methods (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1981) and refined (based on F) by full-matrix least-squares calculations with *SHELXTL-Plus*, PC version (Siemens, 1990). H atoms on the benzene ring were fixed (C—H = 0.96 Å) and refined with fixed isotropic thermal parameters. The methyl groups [C(10) and C(11)] were found to be rotationally disordered. Two separate sets (A, B, C and D, E, F) of H atoms were attached to each methyl C atom and geometrically constrained to maintain tetrahedral geometry (C—H and H⋯H distances within each group were fixed). They were given common isotropic thermal parameters and refined as two rigid groups whose occupancy values were allowed to vary. The populations of the C(10) and C(11) methyl groups

converged at 45/55 and 43/57%, respectively. All other non-H atoms were refined anisotropically. Final residuals were $R = 0.0349$ and $wR = 0.0520$ for 1165 observed reflections. Final residuals for all data were $R = 0.0370$ and $wR = 0.0645$. The quantity minimized was $\Sigma w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0143F^2$. The goodness of fit was 0.46 and the largest and mean Δ/σ values were 0.014 and 0.002, respectively. The data-to-parameter ratio was 5.5:1. The final difference Fourier map exhibited maximum and minimum peaks of 0.16 and -0.22 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic coordinates and equivalent isotropic displacement coefficients are given in Table 1* and bond distances and angles are given in Table 2. An *ORTEP* (Siemens, 1990) diagram is shown in Fig. 2. From the crystal structures of BBT, CBODT and NBODT, it is apparent that the preferred conformation of the triazole ring with respect to the carbonyloxy group is nearly orthogonal. A comparison of these structures reveals that the triazole ring is rotated in the opposite sense in NBODT to that in BBT and CBODT. Coplanarity of the triazole ring and the benzoyloxy group would be expected to be prohibited owing to both electronic and steric factors. Electron-pair repulsion of the N(1) and O(1) lone pairs is expected to result in maximum electronic destabilization when the planes of the triazole

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ring and benzoyloxy groups are parallel. In addition, coplanarity of the triazole ring and the benzoyloxy group would be expected to result in destabilizing steric interactions between either N(2) and O(2) [when the N(2)—N(1)—O(1)—C(3) torsion angle is 0°] or between C(11) and O(2) (when the torsion angle is 180°). Interatomic distance measurements, using $AM1$ optimized geometries [with the N(2)—N(1)—O(1)—C(3) torsion angle constrained to 0 or 180°] indicated an N(2)···O(2) distance of 2.78 Å (sum of van der Waals radii = 2.94, $\Delta = 0.16$ Å) when the torsion angle is 0°, and an N(2)···C(11) distance of 2.68 Å (sum of van der Waals radii = 3.3, $\Delta = 0.62$ Å). The difference in the magnitude of these steric interactions is reflected in the difference in calculated heats of formation for these rotamers (Fig. 1).

Full geometry-optimization $AM1$ calculations were also performed on all three compounds using X-ray coordinates as starting geometries. The $AM1$ and X-ray geometries are compared using $MACRO-MODEL$ (Still, 1990) in Fig. 3. The calculated and observed structures are similar but differ somewhat
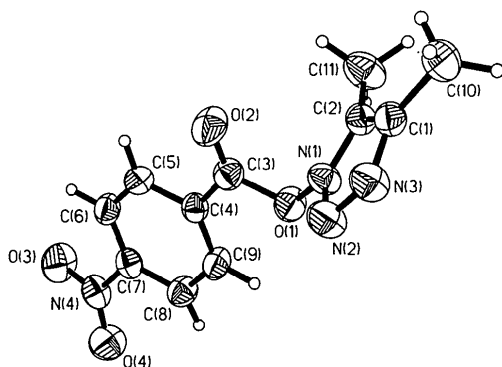

Fig. 2. An $ORTEP$ diagram of NBODT showing the atomic numbering scheme. Disordered H atoms attached to C(10) and C(11) have been omitted for clarity.
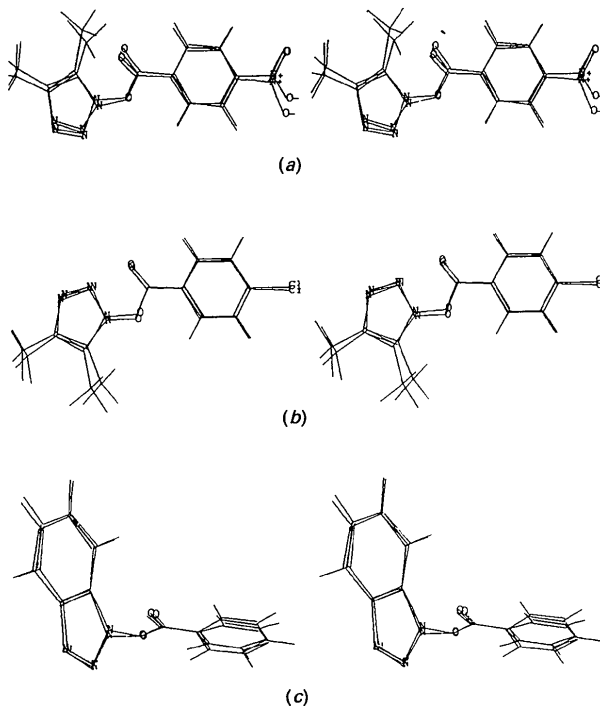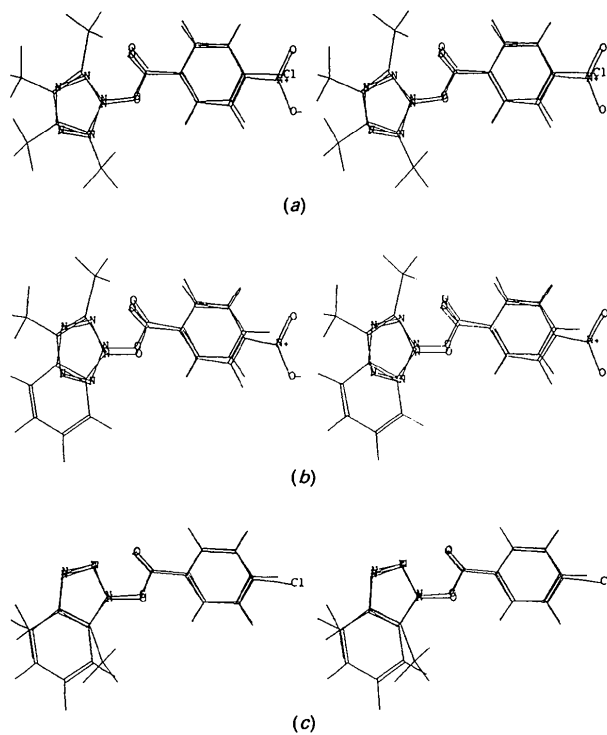

Fig. 4. Stereographic comparisons (r.m.s. deviations) of X-ray structures for: (a) NBODT/CBODT (0.185 Å); (b) NBODT/BBT (0.243 Å); (c) CBODT/BBT (0.082 Å).
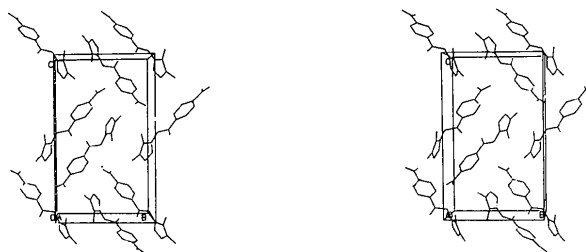

Fig. 3. Stereographic comparisons with calculated r.m.s. deviations of X-ray and $AM1$ structures for: (a) NBODT, r.m.s. = 0.227 Å; (b) CBODT, r.m.s. = 0.177 Å; (c) BBT, r.m.s. = 0.233 Å.

Fig. 5. A stereographic view of the crystal packing viewed along the crystallographic a axis.

in bond angle and torsional parameters. Fig. 4 illustrates a similar geometrical comparison of the X-ray crystal structures of all three substances and Fig. 5 is a stereographic view of the crystal packing.

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Structure of Pentafluorophenyl Isocyanide at 115 K

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Abstract. C_7F_5N, $M_r = 193.08$, orthorhombic, *Cmca*, $a = 7.611$ (3), $b = 9.427$ (5), $c = 18.603$ (14) Å, $V = 1334$ Å^3, $Z = 8$, $D_x = 1.92$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.56$ cm^{-1}, $F(000) = 752$, $T = 115$ (5) K, $R = 0.053$, $wR = 0.050$ for 67 variables and 863 unique reflections for which $F_o > 6\sigma(F_o)$. Pentafluorophenyl isocyanide is an almost planar molecule. The molecular plane made up of the six phenyl C atoms is perpendicular to the crystallographic mirror plane (at $x = 0$) which bisects the phenyl ring and the isocyano group. The C—C bond lengths in the aromatic ring are almost identical, as are the C—F bond lengths. The isocyano moiety is almost linear.

Introduction. In contrast to the extensive structural information available on isocyanide complexes there are only a few isocyanides which have been structurally characterized by X-ray crystallography, electron diffraction or microwave spectroscopy. The only fluorinated isocyanides known thus far are trifluoromethyl isocyanide (Lentz, 1984, and references therein) and pentafluorophenyl isocyanide (Lentz, Graske & Preugschat, 1988), which tend to polymerize readily.

Experimental. Crystals of pentafluorophenyl isocyanide were prepared by reaction of dibromo-*N*-(pentafluorophenyl)methanimine with magnesium in tetrahydrofuran (Lentz, Graske & Preugschat, 1988). Crystals were grown by sublimation at 253 K (melting point with decomposition 286 K) ₁in an evacuated Schlenk tube. A colourless crystal, 0.4 × 0.5 × 0.4 mm, was mounted on the end of a glass fibre using a procedure described by Veith & Bärnighausen (1974) modified by Schumann, Genthe, Hahn, Hossain & van der Helm (1986). Enraf–Nonius CAD-4 diffractometer, unit-cell data from 25 reflections with $9 < \theta < 17°$. $2 \le \theta \le 30°$, ω/θ scan, $\Delta\omega = (1.1 + 0.35\tan\theta)°$, scan speed 1–5° min^{-1}, with $0 \le h \le 10$, $0 \le k \le 12$, $0 \le l \le 25$ and $-22 \le l \le 25$ for $0kl$ reflections, 1224 measured reflections, 990 unique reflections ($R_{int} = 0.018$) of which 863 had $F_o > 6\sigma(F_o)$. Two intensity-control reflections ($\overline{1}54$, $\overline{2}48$) were measured with F_o 80 (1), 74 (1) and showed no change during data collection. The data were not corrected for extinction or absorption and the structure was solved by direct methods (*SHELXS*86; Sheldrick, 1985). All atoms were refined with aniso-tropic displacement parameters by full-matrix least-squares techniques based on F. The refinement mini-