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Structure of Dinaphtho[1,2-*b*:2',1'-*d*]furan, C₂₀H₁₂O

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Abstract. $M_r = 268.32$, monoclinic, $P2_1/c$, $a = 14.309$ (3), $b = 4.665$ (1), $c = 20.827$ (5) Å, $\beta = 109.30$ (2)°, $V = 1312.1$ (9) Å³, $Z = 4$, $D_x = 1.36$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.766$ cm⁻¹, $F(000) = 560$, $T = 294$ K, $R(F) = 0.072$ for 2672 reflections. The dinaphthofuran molecule is non-planar, but displays near twofold symmetry with respect to an axis passing through the O atom and the center of the C(10)–C(20) bond. The C(10)–C(20) bond has a length of 1.438 (3) Å, identical to that found for the corresponding bond in dibenzofuran.

Introduction. The study of dilutely substituted aromatic molecular triplet states by low-field electron paramagnetic resonance spectroscopy is facilitated by knowledge of the crystal structures of the compounds of interest. The crystal structure of dinaphtho[1,2-*b*:2',1'-*d*]furan was determined in part in anticipation of the use of this compound as a host material for such experiments.

Experimental. Dinaphthofuran was synthesized from α -naphthol by the method of Clemo & Spence (1928). The product was a white solid, melting between 457 and 458 K. The identity of the compound was confirmed by ¹H and ¹³C NMR. Clear, acicular crystals grown from acetone featured prominent {100}, {102}, and {10 $\bar{2}}$ faces and easily fractured along [010].

Crystal 0.12 × 0.25 × 0.65 mm mounted along the needle axis (*b*) on a Syntex P $\bar{1}$ diffractometer. Unit-cell parameters and the orientation matrix obtained from a least-squares fit of the setting angles for 22 reflections with 20° < 2 θ < 30°. Intensity data collected for 3815

reflections with +*h*, +*k*, \pm *l* and 4° < 2 θ < 55°, using graphite-monochromated Mo *K* α radiation. Six standard reflections measured after every 94 reflections, maximum intensity variation $\pm 4.5\%$. Space group established by systematic absences. Multiplicative absorption correction factors applied to the F_o 's using the program *DIFABS* (Walker & Stuart, 1984); max. and min. correction factors 1.13 and 0.72, respectively. Averaging of equivalent reflections gave 2791 independent reflections, $R_{\text{int}} = 0.029$. Structure solved using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinement by full-matrix least squares, using *SHELX76* (Sheldrick, 1976) to minimize $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$ for 2672 reflections with $F > 0$. Neutral-atom scattering factors for C and O from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). H-atom positions determined from an electron density difference map, and refined isotropically. Final refinement cycle: 238 variables, $R = 0.072$, $wR = 0.043$, $w = 1/\sigma^2(F)$, $S = 1.4$, $(\Delta/\sigma)_{\text{max}} = 0.2$. Max. and min. peak heights in final $F_o - F_c$ map 0.19 and -0.20 e Å⁻³.

Discussion. The final atomic coordinates and temperature factors for dinaphthofuran are given in Table 1.* Bond lengths and angles, calculated using *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), are shown in Figs. 1(*a*) and 1(*b*), respectively. There are

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42037 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses

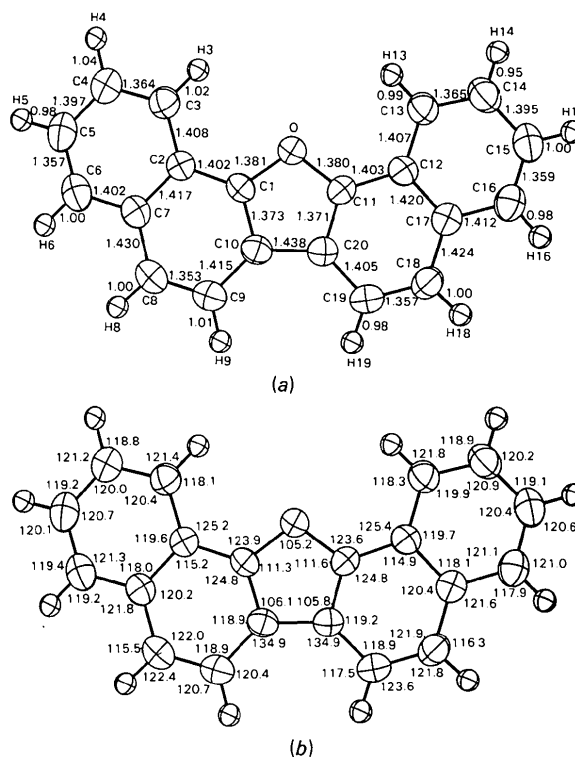
Values are multiplied by 10^4 for non-hydrogen atoms and by 10^3 for all H atoms. Equivalent isotropic temperature factors were calculated using the equation $U_{\text{eq}} = \frac{1}{3}(\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j)$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U_{iso}
O	1953 (1)	4510 (2)	3206 (1)	443 (4)
C(1)	2006 (1)	3213 (4)	3813 (1)	399 (5)
C(2)	1311 (1)	1223 (4)	3882 (1)	413 (5)
C(3)	467 (1)	294 (4)	3352 (1)	497 (6)
C(4)	-165 (2)	-1651 (4)	3477 (1)	574 (7)
C(5)	18 (2)	-2702 (5)	4135 (1)	662 (8)
C(6)	823 (2)	-1824 (5)	4655 (1)	590 (7)
C(7)	1493 (1)	166 (4)	4550 (1)	458 (6)
C(8)	2342 (2)	1112 (4)	5095 (1)	535 (7)
C(9)	2991 (2)	3027 (4)	4996 (1)	506 (7)
C(10)	2828 (1)	4105 (4)	4333 (1)	411 (6)
C(11)	2771 (1)	6280 (4)	3361 (1)	404 (5)
C(12)	2994 (1)	8019 (4)	2881 (1)	398 (5)
C(13)	2427 (2)	8215 (4)	2187 (1)	508 (7)
C(14)	2727 (2)	9973 (5)	1769 (1)	593 (8)
C(15)	3588 (2)	11607 (5)	2021 (1)	616 (8)
C(16)	4145 (2)	11467 (4)	2690 (1)	557 (7)
C(17)	3875 (1)	9655 (4)	3142 (1)	445 (6)
C(18)	4462 (1)	9455 (4)	3842 (1)	540 (7)
C(19)	4203 (1)	7737 (4)	4281 (1)	493 (6)
C(20)	3331 (1)	6105 (4)	4036 (1)	412 (5)
H(3)	35 (1)	110 (4)	288 (1)	68 (6)
H(4)	-78 (1)	-231 (4)	308 (1)	84 (7)
H(5)	-43 (1)	-414 (4)	422 (1)	78 (6)
H(6)	94 (1)	-259 (4)	512 (1)	62 (6)
H(8)	244 (1)	20 (4)	555 (1)	61 (5)
H(9)	359 (1)	365 (4)	538 (1)	76 (6)
H(13)	182 (1)	705 (4)	202 (1)	63 (6)
H(14)	232 (1)	1013 (4)	130 (1)	69 (6)
H(15)	378 (1)	1289 (4)	170 (1)	70 (6)
H(16)	475 (1)	1261 (4)	287 (1)	62 (6)
H(18)	507 (1)	1065 (4)	399 (1)	66 (6)
H(19)	460 (1)	755 (4)	477 (1)	58 (5)

two different kinds of C—C bonds in the naphthalene subunits, as would be expected on the basis of the three most stable resonance structures of the naphthalene molecule. The average values for these two bond lengths are 1.363 and 1.410 \AA , comparable with the average values 1.367 \AA and 1.418 \AA for the same bonds in *N*-(2'-pyridyl)-8,13-dioxodnaphtho[2,1-*b*:2',3'-*d*]furan-6-carboxamide (Goldstein, 1975). The C(10)—C(20) and O—C bond lengths, 1.438 (3) and 1.381 (2) \AA , are in agreement respectively with the values 1.438 (3) \AA and 1.384 (1) \AA found for the corresponding bonds in dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984).

The dinaphthofuran molecule is not planar, the mean planes of the two naphthalenic groups being inclined with respect to the mean plane of the five-membered ring at approximately equal but opposite angles. The dihedral angle between the mean planes of the naphthalenic groups is 1.0°. All atomic positions in the molecule, except for C(4) through C(6) and C(14) through C(16), exhibit near twofold symmetry with respect to a non-crystallographic axis which passes through the O atom and the center of the C(10)—C(20) bond. The positions of the six atoms mentioned above deviate only slightly from the pseudo-twofold symmetry, possibly due to the inequivalence of the environment at the two ends of the molecule.

A stereoview of the unit cell is shown in Fig. 2. The closest intermolecular contact distance, 2.32 (3) \AA , occurs between H(5) and H(6) atoms and is consistent with the expected separation based on van der Waals radii.



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Structure of the 1/1 Complex between Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), $C_4H_8N_8O_8$, and *N*-Methyl-2-pyrrolidinone (NMP), C_4H_9NO

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Abstract. HMX–NMP, $M_r = 395.1$, hexagonal, $R\bar{3}c$, $a = 16.607(4)$, $c = 31.506(8)$ Å, $V = 7525.2(38)$ Å³, $Z = 18$, $D_x = 1.570$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.28$ cm⁻¹, $F(000) = 3744$, $T = 298$ K, $R_F = 0.085$ with a goodness-of-fit of 1.887 for those 1287 reflections with $F_o > 5\sigma(F_o)$ and 114 parameters. The structure of HMX–NMP consists of HMX molecules in the chair–chair ring conformation and twofold disordered NMP molecules, a situation comparable to that found for HMX–DMF. Bond distances and angles in HMX are regular and normal. The closest HMX–HMX contact is 3.016(7) Å.

Introduction. The energetic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, $C_4H_8N_8O_8$, known as HMX, stoichiometrically cocrystallizes with a variety of organic molecules having appropriate size, shape, and polarity (George, Cady, Rogers & Rohwer, 1965; Selig, 1982). In fact, the physical and chemical properties of HMX might be tailored systematically by such dopants. A desire to learn how nitramines accommodate other molecules in their crystal lattice prompted us to determine the structure of HMX–*N,N*-dimethylformamide (DMF) (Haller, Rheingold & Brill, 1983) which had been reported earlier (Cobbedick & Small, 1975). However, our sample contained two distinctly different crystal habits, one of which

matched the space group $R\bar{3}c$ (Cobbedick & Small, 1975), and the other of which had major violations to rhombohedral symmetry. Both structures were found to be very similar. Marsh (1984) believes them to be the same and we have not been able to resolve the problem satisfactorily. The structure of the 1/1 complex of hexahydro-1,3,5-trinitro-*s*-triazine with sulfolane has also recently been described (Haller, Brill & Rheingold, 1984). We expand this subject now with the structure of the 1/1 complex between HMX and *N*-methyl-2-pyrrolidinone (NMP).

Experimental. A crystal (0.26 × 0.32 × 0.38 mm) of HMX–NMP, grown by slow cooling of a saturated NMP solution of HMX, was epoxied to a glass fiber and coated with varnish to prevent solvent loss. Data collected on a Nicolet R3 automated diffractometer, graphite monochromator. 25 reflections used to refine orientation matrix. No absorption correction. Systematic absences are hkl : $-h + k + l = 3n + 1, 3n + 2$; $h\bar{h}0l$: $l = 2n + 1$; possible space groups $R\bar{3}c$ ($\bar{3}m$) and $R3c$; $R\bar{3}c$ chosen by E statistics and later confirmed by successful solution and refinement. 5833 reflections scanning ω ($3^\circ \leq 2\theta \leq 43^\circ$) at 3.5° min⁻¹; limits: $h = 0-18$, $k = 0-\pm 18$, $l = 0-\pm 33$; $R_{\text{merge}} = 0.0212$; 2048 unique, 1287 observed with $F_o \geq 5\sigma(F_o)$; 114 parameters. 3 check reflections measured every 141 reflections, no decay. *SHELXTL* direct methods *SOLV* (Sheldrick, 1981). Blocked-cascade procedure.

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