Crystal Structure of the Red-Orange
1-(p-Nitrophenyl)-2-(2,5-dimethylpyrryl)-1,3-propanediol

Merton D. Baird*[1a] and Herman L. Ammon[1b]

*Departments of Chemistry, Shippensburg State College, Shippensburg, Pennsylvania 17257
and University of Maryland, College Park, Maryland 20742*

The three-dimensional X-ray crystal structure of the title compound (REDPYR) was determined to investigate the possibility that intramolecular effects were responsible for its bright red-orange color. The crystal data are: monoclinic, $P2_1$; $a = 9.822$ (2), $b = 10.859$ (2), $c = 6.9271$ (8) Å, $\beta = 97.99$ (2)°. Intensity data were measured with Mo radiation with a diffractometer. The structure was solved with direct methods and refined with full-matrix least-squares techniques to $R = 0.039$. The molecular conformation in the crystal shows the presence of an intermolecular nitro–pyrrole π-type interaction and eliminates the possibility of an intramolecular σ-type interaction between OH and the nitroaromatic ring. Visible spectra of the title compound and of binary solutions of the separate aromatic chromophores are reported.

The condensation of *threo*-2-amino-1-(*p*-nitrophenyl)-1,3-propanediol and 2,5-hexanedione was reported[2] to give the bright red-orange compound 1-(*p*-nitrophenyl)-2-(2,5-dimethylpyrryl)-1,3-propanediol (I) along with the colorless 1,7-dimethyl-*exo*-3-(*p*-nitrophenyl)-2,6-dioxa-10-azatricyclo[5.2.1.0[4,10]] decane. It was proposed that the color of I was due either to a σ-type charge transfer complex between the *p*-nitrophenyl and pyrryl moieties or to a σ-type charge transfer complex (II) between the *p*-nitrophenyl ring and the

I   II
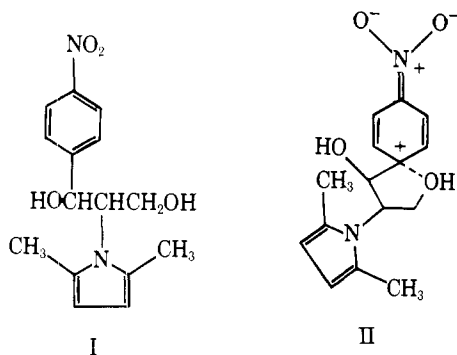
oxygen of the 3-hydroxy group. In an attempt to identify the molecular basis for the color of I (herein called REDPYR), we have determined its crystal structure and studied the visible spectra of the material and of solutions of compounds containing the pyrryl and *p*-nitrophenyl moieties. These results are reported here.

Discussion

The structure of REDPYR in the crystal is illustrated with an ORTEP drawing in Figure 1. The conformation about the C(1)–C(2) bond is almost perfectly staggered, with, for example, a 178° dihedral angle between the pyrryl nitrogen on C(2) and the first phenyl carbon atom on C(1). Other dihedral angles are listed in Table I. In addition to the low-energy, antiperiplanar orientation of the benzene and pyrrole moieties, the two rings are almost parallel to each other, differing by only 9°, and almost perpendicular to the N(2)–C(2)–C(1)–C(B1) plane, differing by an average of 3° from the four-atom plane. These slight twist angles, which may be due to intramolecular forces, most probably are caused by crystal packing interactions. The C(1)–C(2)–C(3)–O(4) conformation is approximately s-trans and arranged to clearly exclude any type of O(4)···C(B1) linkage, such as that suggested in structure II. An s-cis conformation for C(2)–C(3), with the same C(1)–C(2) conformation shown in Figure 1 and the same bond angles at C(1), C(2), and C(3), would place O(4) about 2.0 Å from C(B1).

Bond lengths and angles are reported in Table II; all values are normal. The nitro and two methyl groups show small deviations from coplanarity with the phenyl and pyrryl rings, respectively; the nitro group is twisted out of the aromatic plane by 10°.

The crystal packing diagram shown in Figure 2 clearly shows one reason for the extension of O(4) in the crystal, viz., the H(O4)···O(3) hydrogen bond between molecules related by the unit translation parallel to c. Also illustrated is the proximate packing of the pyrryl rings and nitro groups. The arrangement is such that each nitro is sandwiched between two pyrroles, and vice versa, with an average nitro–pyrrole distance of 3.39 Å, and a minimum of 3.23 Å. This separation is slightly less than the typical 3.4 Å van der Waals[3] approach between parallel-stacked aromatic rings, and it seems probable that the deep red-orange color of the REDPYR crystals originates in the nitro–pyrrole interaction.

The visible spectra of REDPYR and of compounds containing the nitrobenzene and pyrrole chromophores were determined (see Figure 3) to further evaluate the possibility of intermolecular color producing interactions. Tetrahydrofuran was the only suitable nonhydroxylic solvent found for REDPYR at the required concentrations. It was observed that the yellow color of solutions of the nitroaromatics arises from a UV band, centered at about 272 nm, which tails into the visible and no visible maxima were observed for any of these compounds at concentrations as high as 1.6 M. The spectra show that binary solutions containing 1,2,5-trimethylpyrrole (TMP) and either nitrobenzene (NB) or *p*-nitrobenzyl alcohol (PNBA) fail to reproduce the color intensity of REDPYR. For example, at 415 nm the binary solutions show an absorbance enhancement of about 9% over that of the nitroaromatic. The absorbance of REDPYR solutions is about three times greater at this wavelength. Although no effect was observed when an equimolar amount of methanol was included in the binary solutions in an attempt to mimic the hydroxylic content of REDPYR, solutions where the concentration of nitroaromatic was ca. 150 times greater than the TMP concentration displayed a dramatic increase in absorbance in the visible region. In fact, a mixture of pure TMP and NB is brilliant orange but displays no visible maximum.

The absence of any significant intramolecular electronic interaction between the nitrobenzene and pyrrole groups in REDPYR is suggested by the similarity in absorbance between REDPYR ($\lambda_{max}^{95\%EtOH}$ 273 nm, ϵ 8700)[4], *threo*-1-*p*-nitrophenyl-2-amino-1,3-propanediol ($\lambda_{max}^{95\%EtOH}$ 274 nm, ϵ 11 200),[4] and *p*-nitrotoluene ($\lambda_{max}^{95\%EtOH}$ 273 nm, ϵ 9300).[5] However, the enhanced visible absorption of dilute REDPYR solutions over that of TMP/PNBA mixtures suggests that the nitrophenyl group in REDPYR is being influenced by the
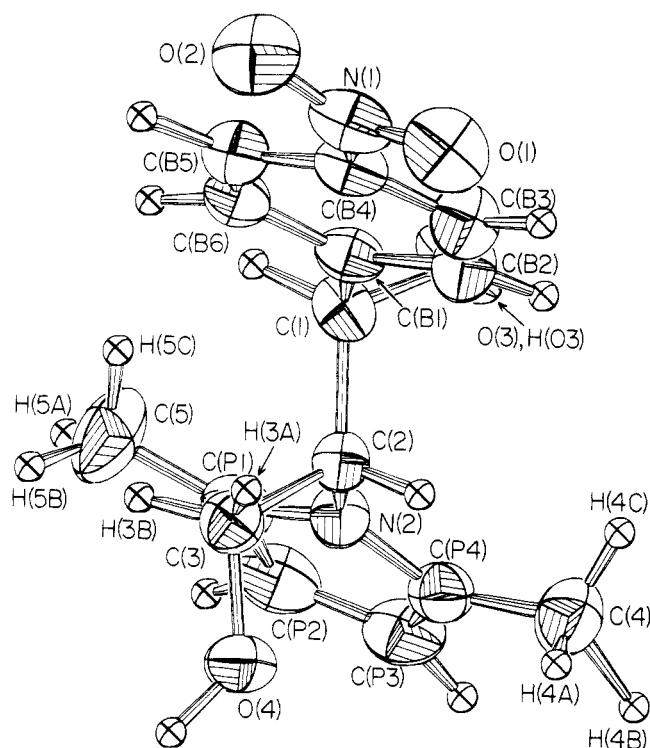
Figure 1. ORTEP drawing of REDPYR. The C, N, and O atoms are depicted as 50% ellipsoids, the H atoms are shown as 0.1 Å radius spheres.

Table II. Bond Lengths (Å), Angles (deg), and esd's (in Parentheses)

C(1)–C(2)	1.536 (6)	C(3)–C(2)–N(2)	112.0 (3)
C(1)–C(B1)	1.515 (5)	C(2)–C(3)–O(4)	110.5 (4)
C(1)–O(3)	1.427 (5)	C(5)–C(P1)–C(P2)	127.9 (5)
C(2)–N(2)	1.467 (4)	C(5)–C(P1)–N(2)	125.7 (4)
C(2)–C(3)	1.529 (6)	C(P2)–C(P1)–N(2)	106.4 (5)
C(3)–O(4)	1.422 (6)	C(P1)–C(P2)–C(P3)	108.1 (4)
C(4)–C(P4)	1.495 (7)	C(P2)–C(P3)–C(P4)	108.1 (4)
C(5)–C(P1)	1.493 (8)	C(4)–C(P4)–C(P3)	128.5 (5)
C(P1)–N(2)	1.398 (6)	C(4)–C(P4)–N(2)	123.4 (4)
C(P1)–C(P2)	1.384 (6)	C(P3)–C(P4)–N(2)	108.0 (5)
C(P2)–C(P3)	1.411 (9)	C(1)–C(B1)–C(B2)	121.5 (4)
C(P3)–C(P4)	1.362 (5)	C(1)–C(B1)–C(B6)	118.6 (4)
C(P4)–N(2)	1.379 (6)	C(B2)–C(B1)–C(B6)	119.9 (3)
C(B1)–C(B2)	1.389 (7)	C(B1)–C(B2)–C(B3)	120.3 (4)
C(B1)–C(B6)	1.390 (7)	C(B2)–C(B3)–C(B4)	118.6 (4)
C(B2)–C(B3)	1.385 (5)	C(B3)–C(B4)–C(B5)	123.0 (3)
C(B3)–C(B4)	1.379 (7)	C(B3)–C(B4)–N(1)	118.9 (4)
C(B4)–N(1)	1.468 (4)	C(B5)–C(B4)–N(1)	118.1 (4)
C(B4)–C(B5)	1.385 (7)	C(B4)–C(B5)–C(B6)	117.4 (4)
C(B5)–C(B6)	1.400 (5)	C(B1)–C(B6)–C(B5)	120.7 (4)
N(1)–O(1)	1.222 (5)	C(B4)–N(1)–O(1)	118.2 (4)
N(1)–O(2)	1.223 (6)	C(B4)–N(1)–O(2)	118.1 (4)
H(O3)–O(3)	0.55 (6)	O(1)–N(1)–O(2)	123.7 (3)
H(O4)–O(4)	1.02 (8)	C(2)–N(2)–C(P1)	126.8 (1)
		C(2)–N(2)–C(P4)	123.7 (4)
C(2)–C(1)–C(B1)	110.8 (3)	C(P1)–N(2)–C(P4)	109.4 (3)
C(2)–C(1)–O(3)	109.3 (4)	H(O3)–O3–C(1)	119 (7)
C(B1)–C(1)–O(3)	108.1 (3)	H(O4)–O4–C(3)	129 (5)
C(1)–C(2)–C(3)	114.1 (4)		
C(1)–C(2)–N(2)	111.8 (3)		

Table I. Dihedral Angles (in degrees) between Atoms on C(1) and C(2)

N(2)–C(2)-C(1)–C(B1)	178	C(3)–C(2)-C(1)–H(1)	66
N(2)–C(2)-C(1)–O(3)	59	H(2)–C(2)-C(1)–C(B1)	60
N(2)–C(2)-C(1)–H(1)	62	H(2)–C(2)-C(1)–O(3)	59
C(3)–C(2)-C(1)–C(B1)	53	H(2)–C(2)-C(1)–H(1)	179
C(3)–C(2)-C(1)–O(3)	173		

molecule's internal environment. A referee proposed the intriguing possibility of a conjugative link between the pyrryl and phenyl π systems via the planar C(B1)–C(1)–C(2)–N(2) σ-bond network.

The large color enhancement observed in solutions containing a large excess of one of the chromophores presumably arises from an intermolecular effect. A similar situation was found for solutions of 4-nitro-4'-dimethylamino-1,2-diphenylethane which show an increase in intensity at long wavelengths when a large excess of one of the chromophores (NB) is present.[6] The precise nature of the intermolecular interactions between π-excessive N-alkyl pyrryl groups and π-deficient p-nitrophenyl groups is not clear at present. Anderson,[7] in a study of NMR solvent shifts on N-methylpyrrole in various solvents, found that the shifts observed in nitrobenzene could be explained by an interaction between the nitro group in the solvent and N-methylpyrrole. A similar type of interaction is indicated for the crystalline state of RED-PYR.

Experimental Section

1-(p-Nitrophenyl)-2-(2,5-dimethylpyrryl)-1,3-propanediol (*I*) was prepared by the acetic acid catalyzed condensation of D-(−)-*threo*-1-(p-nitrophenyl)-2-amino-1,3-propanediol and 2,5-hexanedione in benzene with the solvent azeotrope method. Bright red-orange block-like crystals were obtained following the addition of ether to the reaction mixture (mp 150.5–152 °C (lit.[2] mp 151–151.5 °C)).

Preliminary X-ray oscillation and Weissenberg photographs (Ni-filtered Cu radiation) were used for space group and approximate cell constant determination. All final X-ray measurements were made on
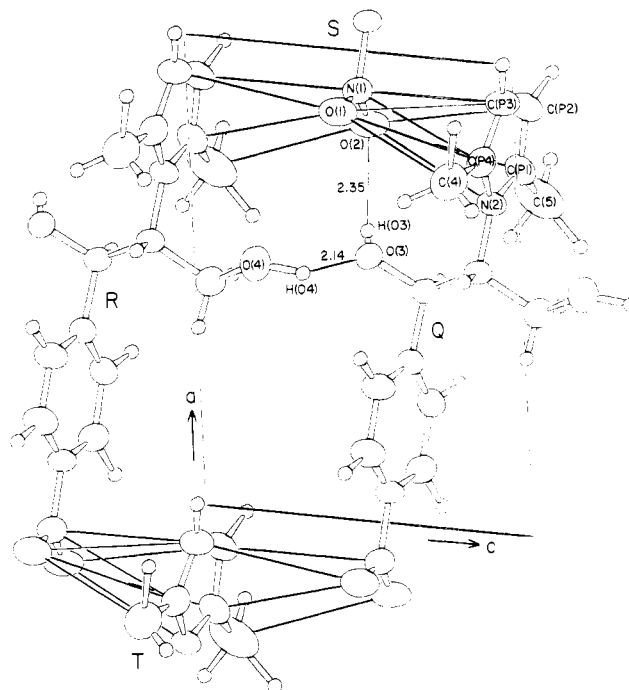

Figure 2. Packing diagram viewed normal to the ac plane. The Q–T designations refer to molecules at: Q = x,y,z; R = x,y,-1 + z; S = 1 + x,y,z; T = −1 + x,y,-1 + z. Intermolecular contact distances (Å) are given in Table III.

a Picker FACS-I diffractometer with monochromatized Mo radiation (highly oriented graphite crystal, Mo Kα λ 0.71069 Å). A 0.1 × 0.3 × 0.4 mm crystal was mounted and aligned to place b* parallel to the diffractomer's φ axis. The cell parameters were determined by the method of least squares from the Bragg angles of 12 reflections manually measured at ±2θ (average $|2\theta_o - 2\theta_c| = 0.003$). The crystal data were: $C_{15}H_{18}N_2O_4$; mol wt 290.3; monoclinic, $P2_1$, a = 9.822 (2), b = 10.859 (2), c = 6.9271 (8) Å, β = 97.99 (2)°; $D_{calcd} = 1.32$ g cm⁻³ for Z = 2. The intensity data were collected with the 0–2θ scan
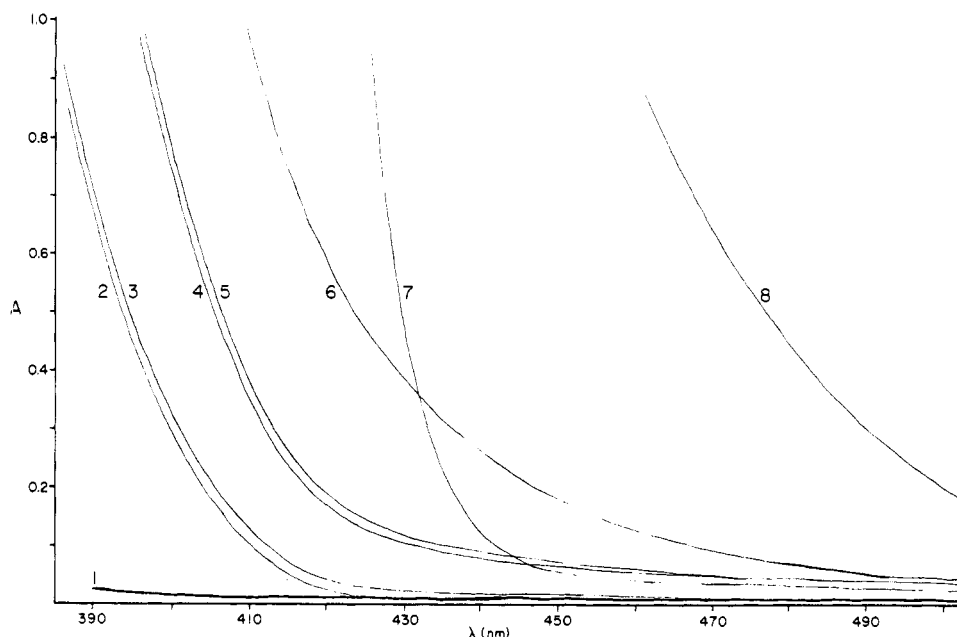
Figure 3. Visible spectra of REDPYR and solutions containing combinations of 1,2,5-trimethylpyrrole (TMP), *p*-nitrobenzyl alcohol (PNBA), and nitrobenzene (NB) in tetrahydrofuran: 1, 0.033 M TMP; 2, 0.033 M NB; 3, 0.033 M NB and 0.033 M TMP; 4, 0.034 M PNBA; 5, 0.034 M PNBA and 0.034 M TMP; 6, 0.034 M REDPYR; 7, 4.89 M NB; 8, 4.90 M NB and 0.033 M TMP.

Table III. Intermolecular Contact Distances, Å

C(P1,Q)–O(2,S)	3.35	N(2,Q)–O(2,S)	3.42
C(P2,Q)–O(2,S)	3.45	O(1,Q)–C(P1,T)	3.49
C(P3,Q)–N(1,S)	3.29	O(1,Q)–C(P2,T)	3.24
C(P3,Q)–O(1,S)	3.47	O(1,Q)–C(P3,T)	3.54
C(P4,Q)–N(1,S)	3.39	O(2,Q)–C(5,T)	3.53
C(P4,Q)–O(1,S)	3.23	O(3,Q)–H(O4,R)	2.14
C(4,Q)–O(1,S)	3.28	O(3,Q)–O(4,R)	2.85
N(1,Q)–C(P2,T)	3.36	O(3,Q)–O(2,S)	2.91
		H(O3,Q)–O(2,S)	2.35 (1.94^a)

^{a} Calculated value when O(3)–H(O3) distance is extended from the observed value of 0.55 Å to a more reasonable value of 0.97 Å.

method, with a 2θ speed of 2° min^{-1}, a 2θ scan range calculated from 1.4 + 0.7 tan θ, and two 10-s background measurements. Three standard reflections measured at 50 reflection intervals were used to monitor and later correct for intensity variations. There were 1372 unique reflections in a total of 1582 data measured to a 2θ maximum of 50°; 1148 of the unique data were more than three standard deviations above background.

The structure was solved with the MULTAN[8] system of programs, and an E map computed with the 276 phases ($E \geq 1.2$) corresponding to the best combined figure of merit revealed maxima for the 21 C, N, and O atoms.

The structure refinement was by the method of full-matrix least squares with anisotropic temperature factors for C, N, and O and isotropic terms for H. The hydrogen atoms were located from a difference map. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$. Only those data for which I_c was greater than $3\sigma(I_o)$ were included in the summation (130 reflections were omitted from the last cycle of least squares on the basis of this criterion). The final $R(\Sigma(|F_o| - |F_c|)/\Sigma F_o)$ and weighed $R([\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2})$ factors were 0.039 and 0.034, respectively.

The calculations were carried out at the University of Maryland's Computer Science Center on a UNIVAC 1108 computer with the X-RAY system of crystallographic programs.[9]

The visible spectra were recorded with a Cary 15 in THF solvent with 0.1 and 1.0-cm cells. Reagent-grade nitrobenzene and *p*-nitrobenzyl alcohol were used without further purification, whereas 1,2,5-trimethylpyrrole was distilled in vacuo to remove a yellow-brown discoloration.

Registry No.—I, 21407-90-9; *D*-(−)-threo-1-(*p*-nitrophenyl)-2-amino-1,3-propanediol, 716-61-0; 2,5-hexanedione, 110-13-4.

Supplementary Material Available. Atomic coordinates and esd's, temperature factors, and bond lengths, angles, and esd's for bonds involving hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Shippensburg State College; (b) University of Maryland.
(2) H. S. Broadbent, W. S. Burnham, R. M. Sheeley, and R. K. Olsen, *J. Heterocycl. Chem.*, **13**, 337 (1976).
(3) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, 1960, p 235.
(4) R. M. Sheeley, Ph.D. Thesis, Brigham Young University, 1964.
(5) W. M. Shubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957).
(6) V. A. Glushenkov, V. A. Izmail'skii, and Yu. Sh. Moshkovskii, *Dokl. Acad. Nauk SSSR*, **153**, 1363–6 (1963).
(7) H. J. Anderson, *Can. J. Chem.*, **43**, 2387 (1965).
(8) P. Main, M. M. Woolfson, L. Lessinger, G. Germain, and J. P. Declercq, "MULTAN, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", 1974, Universities of York, England and Louvain-La-Neuve, Belgium.
(9) X-RAY System of Crystallographic Programs (1976). Edited by J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, Technical Report 446, Computer Science Center, University of Maryland.