The Crystal Structures of the *syn*- and *anti-p*-Bromobenzophenone Oxime *O*-Picryl Ethers[1]

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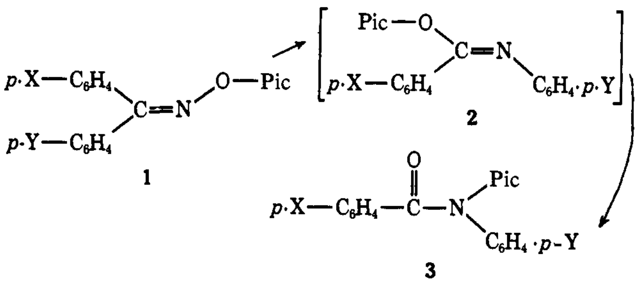
Abstract: The crystal structures of the *syn*- and *anti-p*-bromobenzophenone oxime *O*-picryl ethers (**1b** and **1c**) have been determined by X-ray diffraction methods to provide information relevant to their solid-state rearrangements. The nearly colorless prisms of **1b** are monoclinic with a = 14.67 (3), b = 7.64 (1), and c = 37.25 (8) Å, β = 107°10′ (10′) with eight molecules in the unit cell; the space group is $P2_1/c$. The structure has been refined to an R factor of 0.15 on the basis of 4931 independent nonzero reflections collected photographically (Cu Kα) at 4°. The nearly colorless prisms of **1c** are monoclinic with a = 12.56 (2), b = 7.95 (2), c = 21.49 (4) Å, and β = 113°43′ (15′) with four molecules in the unit cell; the space group is $P2_1/c$. The structure has been refined to an R factor of 0.062 on the basis of 3038 independent nonzero reflections collected on a diffractometer (Cu Kα radiation) at ambient room temperature. Cell data are presented for the parent benzophenone oxime *O*-picryl ether (**1a**) and for the products (**3a–c**) of the rearrangements of **1a–c**. There are no startling differences in the molecular geometry of the two conformers of **1b** and of the molecule of **1c**. In the crystal of **1c**, the oxygen and the two ortho nitrogen substituents on the picryl ring are displaced from the plane of the picryl ring by −0.095, 0.144, and −0.134 Å. There is considerable evidence for intramolecular overcrowding in this region of the molecule. The phenyl ring syn to the *O*-picryl group is rotated by 60.5° out of the best plane through the central five-atom ($C_2C{=}N({-}O)$) group in the molecule, while the other phenyl ring is only rotated by 18.6°. The C–N (oxime), N–O (ether), and C(picryl)–O(ether) lengths are 1.291 (6), 1.441 (5), and 1.349 (5) Å. The intramolecular distances between the migrating oxygen atom and the carbon atom to which it migrates are 2.213 (5), 2.25 (2), and 2.23 (2) Å in **1c** and the two molecules of **1b**; there are no intermolecular contacts between these atoms less than 4 Å.

The benzophenone oxime *O*-picryl ethers (**1a–c**) undergo Beckmann rearrangements in solution to form *via* the intermediates **2a–c** the respective *N*-picrylanilides (**3a–c**).[4] Crystals of **1a–c** were observed to undergo reaction upon heating and the products were shown to be **3a–c**.[5] A crystallographic investigation of compounds **1a–c** and **3a–c** was undertaken to provide information on the lattices and molecular geometries of the reactants and products of this potentially solid-state reaction. Unit cell dimensions and space groups were determined for all six compounds and full three-dimensional structure analyses were carried out on compounds **1b** and **1c**. The structure of the *syn-p*-bromobenzophenone oxime *O*-picryl ether (**1b**) was determined from visually estimated data collected photographically, while that of the *anti-p*-bromobenzophenone oxime *O*-picryl ether (**1c**) was determined from data measured on an automatic diffractometer.



a, X = Y = H
b, X = Br; Y = H
c, X = H; Y = Br

Experimental Section

The preparation and purification of the oxime *O*-picryl ethers (**1a–c**) and of their rearrangement products (**3a–c**) are described in another paper in this series.[5]

Crystal Data. Cell parameters were determined on a precession camera fitted with a Polaroid casette and using Mo Kα radiation (λ = 0.7107 Å) at 25 ± 5°, unless otherwise stated. The densities were determined by flotation in aqueous zinc chloride.

Benzophenone Oxime *O*-Picryl Ether (1a). The nearly colorless plates, with a prominent diamond-shaped face, of **1a** (mol wt = 408.33) were obtained from an acetone–petroleum ether mixture. The crystals are monoclinic with a = 11.70 (2), b = 12.83 (5), and c = 25.49 (7) Å, β = 90°0′ (10′), V = 3826 (32) Å^3, ρ_{measd} = 1.40 g cm^{-3}, Z = 8, ρ_{calcd} = 1.42 g cm^{-3}; space group $C2/c$ or Cc. The number of molecules in the unit cell and the probable site symmetry of the molecule strongly favor $C2/c$ as the correct group. The prominent face on the crystals is (0 0 1) with the a and b axes corresponding to the diagonals of this face.

***syn-p*-Bromobenzophenone Oxime *O*-Picryl Ether (1b).** The nearly colorless prisms of **1b** (mol wt = 487.22) were obtained from an acetone–petroleum ether mixture. The crystals are usually elongated in the b direction with a number of prominent faces in the [0 1 0] zone. The crystals are monoclinic with a = 14.67 (3), b = 7.64 (1), and c = 37.25 (8) Å, β = 107°10′ (10′), V = 3989 (22) Å^3, ρ_{measd} = 1.62 g cm^{-3}, Z = 8, ρ_{calcd} = 1.62 g cm^{-3}, space group $P2_1/c$, $F(0\,0\,0)$ = 1952, μ (Cu Kα) = 35.7 cm^{-1}. The cell dimensions were also measured at 2 ± 2° (the temperature of data collection) but did not show significant differences from the above values.

***anti-p*-Bromobenzophenone oxime *O*-picryl ether (1c)** forms crystals with two distinct habits. Colorless prisms quite similar to those formed by **1b** are obtained from acetone–petroleum ether; these crystals are also elongated along the b axis. In addition, **1c** also crystallizes as thin hexagonal-shaped plates with well-developed (1 0 0) faces. The unit cell dimensions and diffraction patterns of the crystals with the different habits are identical. The crystals of **1c** (mol wt = 487.22) are monoclinic with a = 12.56 (2), b = 7.96 (2), and c = 21.49 (4) Å, β = 113°43′ (15′), V = 1967 (12) Å^3,

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[1] Taken from the Ph.D. Thesis of J. D. McCullough, Jr., submitted to the University of Illinois, Urbana, Ill., 1970.

[2] National Institutes of Health Predoctoral Trainee, 1968–1970. We are also indebted to the National Science Foundation and the National Institutes of Health for grants partially supporting this work.

[3] Alfred P. Sloan Research Fellow, 1968–1970.

[4] A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936); A. W. Chapman and C. C. Howis, *ibid.*, 806 (1933); A. W. Chapman, *ibid.*, 1550 (1934).

[5] J. D. McCullough, Jr., D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 874 (1972).

ρ_{measd} = 1.64 g cm^{-3}, Z = 4, ρ_{calcd} = 1.66 g cm^{-3}, space group $P2_1/c$, $F(0\ 0\ 0)$ = 976, μ (Cu Kα) = 36.2 cm^{-1}. These cell data were calculated from the orientation matrix used to collect intensity data on the diffractometer. They agreed within the estimated standard deviations with those obtained from precession photographs.

***N*-Picrylbenzanilide (3a)** crystallizes as yellow prisms, elongated in the *b* direction, from acetone. The crystals of **3a** (mol wt = 408.33) are monoclinic, a = 11.55 (3), b = 6.12 (1), and c = 26.19 (6) Å, β = 100°50′ (10′), V = 1817 (12) Å^3, ρ_{measd} = 1.46 g cm^{-3}, Z = 4, ρ_{calcd} = 1.49 g cm^{-3}, space group $P2_1/c$.

***N*-Picryl-*p*-bromobenzanilide (3b)** crystallizes as yellow diamond-shaped plates from an acetone-petroleum ether mixture. The crystals of **3b** (mol wt = 487.22) are monoclinic, a = 14.57 (4), b = 8.77 (1), and c = 15.51 (3) Å, β = 106°15′ (10′), V = 1903 (11) Å^3, ρ_{measd} = 1.69 g cm^{-3}, Z = 4, ρ_{calcd} = 1.70 cm^{-3}. The space group is $P2_1/c$.

***N*-(Picryl)benz-*p*-bromoanilide (3c)** crystallizes as yellow plates with apparent *mmm* morphological symmetry from an acetone–petroleum ether mixture. The crystals of **3c** (mol wt = 487.22) are orthorhombic, a = 13.94 (3), b = 15.04 (5) and c = 18.64 (4) Å, V = 3908 (30) Å^3, ρ_{measd} = 1.63 g cm^{-3}, Z = 8, ρ_{calcd} = 1.66 g cm^{-3}. The space group is either *Pnma* (no. 62) or $Pn2_1a$ (no. 33); the apparent morphological symmetry, the number of molecules in the cell, and the greater prevalence of *Pnma* when compared to $Pn2_1a$ make it the more likely choice.

Structure Analyses. *syn*-*p*-Bromobenzophenone Oxime *O*-Picryl Ether (1b). Data Collection. A crystal of **1b** measuring 1.2 mm along the *b* axis and with a 0.3 × 0.4 mm cross section was mounted along the *b* axis and multiple film equiinclination Weissenberg photographs of the levels *h*0*l* to *h*6*l* were taken with Cu Kα radiation at 2 ± 2°. Visual estimates provided a total of 4931 independent nonzero intensities, which were corrected for Lorentz, polarization, and spot-shape effects, but not for absorption. The seven levels of data were scaled initially on the basis of exposure time. Although the crystal darkened substantially during the period of the data collection, its extinction behavior did not change.

Structure Determination and Refinement. The structure was solved by the heavy atom method. When all 62 nonhydrogen atoms (two molecules) in the crystal asymmetric unit were included in a structure factor calculation, the crystallographic R factor, $R = \Sigma||F_{\text{obsd}}| - |F_{\text{calcd}}||/\Sigma|F_{\text{obsd}}|$, was 0.29. As the number of positional and isotropic thermal parameters exceeded the maximum number permitted in our full-matrix least-squares program by the size of the computer memory, the atoms in the structure were divided into three groups and refined in turn. The weighting scheme used had $\sqrt{w} = 50.0/|F_{\text{obsd}}|$, when $|F_{\text{obsd}}| \geq 50.0$, and $\sqrt{w} = |F_{\text{obsd}}|/50.0$, when $|F_{\text{obsd}}| < 50.0$; the quantity minimized was $\Sigma w||F_{\text{obsd}}| - |F_{\text{calcd}}||^2$. Two full cycles of such refinement reduced R to 0.19 on all observed data. Inclusion of positional and anisotropic thermal parameters for the bromine atoms in the least-squares refinement, along with positional and isotropic thermal parameters for the other nonhydrogen atoms and this time refining the parameters of the two bromine atoms with those of the other atoms in each molecule in turn, gave a final R factor on all the observed data of 0.15.[6] In the last refinement, the final shifts were always less than one-half of the esd in the parameters. Apart from some peaks (~2 e/Å^3) within 2 Å of the bromine atoms, a final difference map did not suggest any significant structural features not included in the structural model. While some of the peaks in the range 0.3–0.5 e/Å^3 could be interpreted in terms of hydrogen atoms, there were other peaks of comparable height that could not reasonably represent hydrogen atoms. Hydrogen atoms, accordingly, were not included in any calculations.

The final values of the positional and thermal parameters are given in Table I. The final list of *h*, *k*, *l*, $|F_{\text{obsd}}|$, and F_{calcd} has been published in the microfilm edition of the Journal.[7] The scattering curves for neutral atoms from the compilation by Ibers[8] were used in the analysis. The curve for bromine was corrected for anomalous dispersion.[9]

Table I. Final Atomic Coordinates (in Fractions of the Unit Cell Edge) and Final Thermal Parameters for **1b** with Estimated Standard Deviations in Parentheses

	x	y	z	B_θ, Å^2
C(1)	0.3337 (8)	0.1387 (17)	0.3284 (3)	1.7 (2)
C(2)	0.3819 (9)	−0.0202 (18)	0.3276 (3)	2.1 (2)
C(3)	0.4119 (10)	−0.0663 (20)	0.2969 (4)	3.1 (3)
C(4)	0.3889 (10)	0.0402 (20)	0.2667 (4)	2.9 (3)
C(5)	0.3406 (11)	0.1995 (21)	0.2663 (4)	3.3 (3)
C(6)	0.3173 (9)	0.2452 (19)	0.2971 (3)	2.2 (2)
C(7)	0.2649 (9)	0.2857 (18)	0.4203 (3)	2.4 (2)
C(8)	0.2952 (10)	0.1267 (21)	0.4346 (4)	3.3 (3)
C(9)	0.3579 (10)	0.1120 (21)	0.4723 (4)	3.1 (3)
C(10)	0.3866 (9)	0.2672 (20)	0.4920 (3)	2.7 (3)
C(11)	0.3565 (10)	0.4303 (20)	0.4782 (4)	3.1 (3)
C(12)	0.2940 (10)	0.4405 (19)	0.4408 (4)	2.7 (3)
C(13)	0.1000 (9)	0.3795 (19)	0.3750 (4)	2.6 (3)
C(14)	0.0520 (10)	0.4526 (20)	0.3416 (4)	3.0 (3)
C(15)	−0.0439 (11)	0.5139 (23)	0.3351 (4)	4.0 (3)
C(16)	−0.0842 (12)	0.5067 (25)	0.3660 (4)	4.4 (4)
C(17)	−0.0324 (12)	0.4358 (24)	0.4000 (5)	4.6 (4)
C(18)	0.0627 (11)	0.3731 (22)	0.4064 (4)	3.8 (3)
C(19)	0.1989 (9)	0.3069 (17)	0.3818 (3)	2.2 (2)
N(20)	0.2152 (7)	0.2533 (16)	0.3514 (3)	2.7 (2)
O(21)	0.3112 (6)	0.1768 (11)	0.3608 (2)	2.2 (2)
N(22)	0.4018 (9)	−0.1416 (18)	0.3592 (3)	3.8 (3)
O(23)	0.3417 (9)	−0.1656 (17)	0.3752 (3)	5.5 (3)
O(24)	0.4770 (9)	−0.2182 (18)	0.3670 (4)	6.0 (3)
N(25)	0.4192 (10)	−0.0041 (21)	0.2333 (4)	4.6 (3)
O(26)	0.4675 (10)	−0.1402 (20)	0.2363 (4)	6.5 (3)
O(27)	0.3924 (10)	0.0817 (20)	0.2060 (4)	6.8 (3)
N(28)	0.2789 (9)	0.4187 (17)	0.2982 (3)	3.4 (2)
O(29)	0.3176 (9)	0.5139 (17)	0.3237 (3)	5.3 (3)
O(30)	0.2110 (10)	0.4598 (20)	0.2718 (4)	6.9 (3)
Br	0.4740 (1)	0.2517 (3)	0.5410 (0)	*a*
C(1′)	0.9268 (9)	−0.0033 (20)	0.3550 (4)	2.8 (3)
C(2′)	1.0235 (10)	−0.0590 (20)	0.3650 (4)	3.3 (3)
C(3′)	1.0724 (11)	−0.0567 (22)	0.3374 (4)	3.8 (3)
C(4′)	1.0301 (11)	0.0201 (22)	0.3050 (4)	3.6 (3)
C(5′)	0.9343 (11)	0.0885 (22)	0.2941 (4)	3.7 (3)
C(6′)	0.8870 (10)	0.0650 (19)	0.3202 (4)	2.8 (3)
C(7′)	0.7783 (9)	−0.1189 (19)	0.4251 (3)	2.4 (2)
C(8′)	0.7265 (11)	−0.2706 (22)	0.4157 (4)	3.6 (3)
C(9′)	0.7515 (12)	−0.4181 (24)	0.4385 (5)	4.4 (4)
C(10′)	0.8282 (10)	−0.4157 (20)	0.4714 (4)	2.9 (3)
C(11′)	0.8785 (12)	−0.2626 (25)	0.4810 (5)	4.6 (3)
C(12′)	0.8548 (12)	−0.1142 (24)	0.4581 (5)	4.2 (3)
C(13′)	0.6705 (9)	0.1440 (18)	0.3978 (3)	2.1 (2)
C(14′)	0.6299 (10)	0.2538 (21)	0.3675 (4)	3.1 (3)
C(15′)	0.5514 (11)	0.3539 (22)	0.3665 (4)	3.5 (3)
C(16′)	0.5114 (10)	0.3503 (21)	0.3974 (4)	3.1 (3)
C(17′)	0.5488 (10)	0.2388 (22)	0.4263 (4)	3.5 (3)
C(18′)	0.6314 (9)	0.1367 (19)	0.4283 (4)	2.6 (3)
C(19′)	0.7544 (9)	0.0345 (19)	0.4001 (4)	2.5 (3)
N(20′)	0.8046 (8)	0.0874 (15)	0.3780 (3)	2.8 (2)
O(21′)	0.8838 (7)	−0.0317 (14)	0.3830 (3)	3.4 (2)
N(22′)	1.0733 (10)	−0.1234 (20)	0.4013 (4)	4.6 (3)
O(23′)	1.0559 (9)	−0.0683 (17)	0.4289 (4)	5.8 (3)
O(24′)	1.1443 (9)	−0.2213 (19)	0.4042 (3)	6.0 (3)
N(25′)	1.0797 (11)	0.0375 (22)	0.2740 (4)	5.2 (3)
O(26′)	1.1529 (10)	−0.0540 (18)	0.2811 (4)	5.9 (3)
O(27′)	1.0472 (11)	0.1363 (23)	0.2494 (5)	7.9 (4)
N(28′)	0.7810 (9)	0.1036 (20)	0.3046 (4)	3.9 (3)
O(29′)	0.7621 (9)	0.2443 (20)	0.2936 (3)	6.1 (3)
O(30′)	0.7283 (9)	−0.0206 (18)	0.3061 (3)	5.3 (3)
Br	0.8591 (1)	−0.6155 (2)	0.5005 (1)	*a*

(× 10^4)	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br	51 (1)	181 (4)	6 (1)	−13 (3)	9 (1)	8 (1)
Br′	66 (1)	161 (4)	9 (1)	91 (4)	19 (1)	27 (1)

[a] Anisotropic temperature factors are expressed in the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

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(6) In view of the large amount of data, refinement of anisotropic thermal parameters for all atoms might have been valid, but the cost that would have been thus incurred was judged to be excessive, when the aim of the analysis, to establish the molecular arrangement within the unit cell, had been accomplished.

(7) These data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(8) J. A. Ibers in "International Tables for X-Ray Crystallography," Volume III, Kynoch Press, Birmingham, England, 1962, pp 201-209.

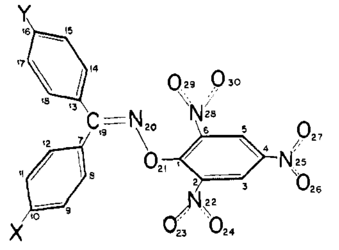
(9) D. H. Templeton in ref 8, pp 213-216.

Table II. Final Atomic Coordinates (in Fractions of the Unit Cell Edge) for **1c**

	x	y	z
C(1)	0.7499 (4)	0.6537 (5)	0.5464 (2)
C(2)	0.8419 (4)	0.6458 (5)	0.5257 (2)
C(3)	0.8645 (4)	0.7703 (6)	0.4878 (2)
C(4)	0.7868 (4)	0.9007 (5)	0.4662 (2)
C(5)	0.6912 (4)	0.9129 (5)	0.4817 (2)
C(6)	0.6760 (4)	0.7915 (5)	0.5236 (2)
C(7)	0.7558 (4)	0.2989 (5)	0.6760 (2)
C(8)	0.8066 (4)	0.1996 (6)	0.6422 (2)
C(9)	0.9079 (5)	0.1127 (7)	0.6793 (3)
C(10)	0.9606 (4)	0.1232 (7)	0.7494 (3)
C(11)	0.9092 (5)	0.2225 (7)	0.7826 (3)
C(12)	0.8080 (4)	0.3078 (6)	0.7464 (2)
C(13)	0.5434 (4)	0.3680 (5)	0.6519 (2)
C(14)	0.4551 (4)	0.4869 (6)	0.6347 (2)
C(15)	0.3607 (4)	0.4645 (6)	0.6509 (2)
C(16)	0.3555 (4)	0.3200 (6)	0.6855 (2)
C(17)	0.4385 (4)	0.1992 (6)	0.7014 (2)
C(18)	0.5336 (4)	0.2223 (6)	0.6850 (2)
C(19)	0.6483 (4)	0.3959 (5)	0.6377 (2)
N(20)	0.6379 (3)	0.5100 (4)	0.5928 (2)
O(21)	0.7491 (3)	0.5296 (4)	0.5890 (2)
N(22)	0.9177 (4)	0.4974 (5)	0.5436 (2)
O(23)	0.8714 (4)	0.3612 (5)	0.5261 (2)
O(24)	1.0222 (3)	0.5204 (5)	0.5720 (2)
N(25)	0.8057 (4)	1.0327 (5)	0.4231 (2)
O(26)	0.8987 (3)	1.0345 (5)	0.4183 (2)
O(27)	0.7261 (4)	1.1301 (5)	0.3947 (2)
N(28)	0.5797 (3)	0.8210 (5)	0.5448 (2)
O(29)	0.4813 (3)	0.8097 (5)	0.5010 (2)
O(30)	0.6052 (3)	0.8627 (5)	0.6035 (2)
Br	0.22877 (5)	0.29035 (8)	0.71091 (3)
H(3)	0.938 (5)	0.777 (8)	0.481 (3)
H(5)	0.636 (5)	1.004 (8)	0.467 (3)
H(8)	0.764 (5)	0.191 (8)	0.594 (3)
H(9)	0.942 (5)	0.048 (8)	0.661 (3)
H(10)	1.046 (5)	0.072 (7)	0.785 (3)
H(11)	0.942 (5)	0.235 (8)	0.829 (3)
H(12)	0.779 (5)	0.363 (8)	0.764 (3)
H(14)	0.466 (5)	0.585 (8)	0.617 (3)
H(15)	0.300 (5)	0.529 (8)	0.639 (3)
H(17)	0.431 (5)	0.092 (8)	0.720 (3)
H(18)	0.590 (5)	0.148 (8)	0.693 (3)

anti-p-**Bromobenzophenone Oxime** ***O*****-Picryl Ether (1c). Data Collection.** A crystal, 0.5 mm in length and 0.2 × 0.2 mm in cross section, was mounted along the elongated b axis on a Picker FACS-1 four-angle diffractometer. Reflections were measured on a scintillation counter with attenuators being inserted when necessary. Approximate monochromatic Cu Kα radiation (λ = 1.54178 Å) was obtained using pulse-height analysis. A 2° peak base width was used, and backgrounds were counted for 10 sec at the upper and lower limits of the 2θ scan. To account for peak broadening with increasing 2θ values a dispersion factor was applied to increase the limits of the 2θ scan. The threshold net count was taken as 0.05 × (total background count), or a net count of 100, whichever was higher. A total of 3339 independent intensities was measured in the 2θ range 0–130° using a moving crystal–moving counter technique at a scan rate of 1°/min. The data were collected at ambient room temperature. Of the 3339 reflections, 3038 were considered to be significantly above the background. No correction was made for absorption or extinction. The intensity of a standard reflection was monitored every 50 measurements, and did not vary by more than 4% during the course of the irradiation. Although the crystal darkened slightly during the data collection period, no change was observed in its extinction behavior.

Structure Determination and Refinement. The coordinates for the one bromine atom in the asymmetric unit were readily determined from a three-dimensional Patterson map. A Fourier map with phases from the bromine atom indicated electron density in reasonable positions for all 31 nonhydrogen atoms. A subsequent structure factor calculation gave an R factor of 0.29. Two cycles of full-matrix least-squares refinement varying positional and isotropic thermal parameters reduced R to 0.17. All nonzero reflections were given unit weight, and the quantity minimized was $\Sigma w||F_{\text{obsd}}| - |F_{\text{calcd}}||^2$. With the introduction of anisotropic thermal parameters for all nonhydrogen atoms, the maximum number of parameters allowed in our least-squares program was exceeded, so refinement was continued by dividing the atoms into two approximately equal groups, C(1)–C(6), N(22), O(23), O(24), N(25), O(26), O(27), N(28), O(29), O(30), in one group and C(7)–C(19), N(20), O(21) in the other, with the bromine atom being common to both groups. Two cycles of full-matrix refinement on each group reduced R to 0.077. A difference map showed reasonable locations for all the hydrogen atoms and some residual electron density elsewhere. The latter included several positive peaks with maxima about three-quarters that of a hydrogen atom in addition to one negative peak with a maximum twice that of hydrogen at the bromine position. The hydrogen atoms and the atoms to which they were bonded were then refined for several cycles. Only the positional parameters were allowed to vary for the hydrogen atoms, the isotropic thermal parameters being held constant at 4.0 Å^2, while the positional and anisotropic thermal parameters were varied for the nonhydrogen atoms. There followed a series of cycles on the two groups divided as above and a final cycle on the hydrogen atoms and attached carbon atoms to produce an R factor of 0.066 and a value of R_2,R_2 = $[\Sigma w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2/\Sigma w|F_{\text{obsd}}|^2]^{1/2}$ of 0.060. Anomalous dispersion corrections[9] were applied to the bromine atom scattering curve, and a further three full cycles of refinement reduced R to 0.062 and R_2 to 0.056 on all nonzero reflections.



1a, X = H, Y = H
1b, X = Br, Y = H
1c, X = H, Y = Br

Figure 1. Sketch of the molecule of **1** showing the atom numbering used in this paper.

The final values of the positional and thermal parameters are given in Tables II and III. The final list of h, k, l, $|F_{\text{obsd}}|$, and F_{calcd} has been published in the microfilm edition.[7] The scattering curves for neutral atoms from the compilation by Ibers[8] were used in the analysis.

Results and Discussion

The atom numbering used in the analysis and in the subsequent discussion is shown in Figure 1. Figure 2 is a stereoscopic view of the conformation of a molecule of **1c**. Bond lengths and angles in the molecule of **1c** are given in Table IV. The results of these X-ray analyses confirm the previous stereochemical assignments to the *p*-bromobenzophenone oximes.[10]

The structure of the anti isomer **1c** will be discussed in somewhat more detail as the results of this analysis are more accurate than those from the syn isomer.[11] If one assumes that the 18 C–C lengths in the three benzene rings are chemically equivalent, then the average C–C (phenyl ring) length is 1.383 Å with a root-mean-square deviation of 0.009 Å. As the average standard deviation (σ) for these bond lengths from the least-squares results is 0.007 Å, a more realistic standard

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(10) A. Schafer, *Justus Liebigs Ann. Chem.*, 264 156 (1891); P. A. S. Smith, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 8.

(11) The 36 independent C–C aromatic distances in **1b** range from 1.32 to 1.44 Å, with a mean value of 1.39 ± 0.03 Å. The other bond lengths agree within the limits of error with those found in **1c**.

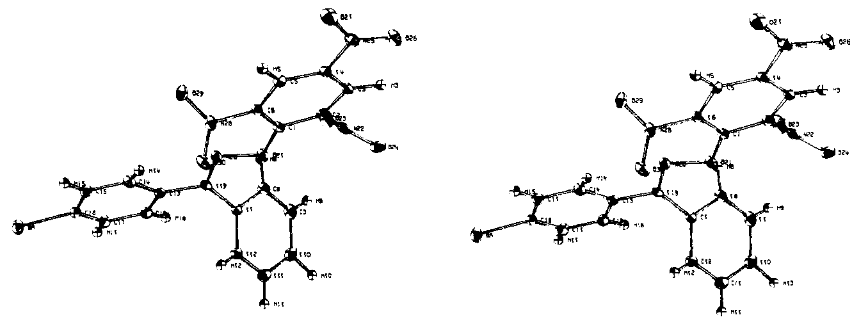

Figure 2. Stereoscopic picture of a single molecule of **1c**.

deviation for the atomic coordinates will therefore be obtained by multiplying σ from the least-squares results by 1.3. The results of some best plane calculations with the atoms weighted by $1/(1.3 \times \sigma)^2$ are given in Table V.

Table III. Final Thermal Parameters for **1c**[a]

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
$\times 10^4$						
C(1)	81 (4)	126 (7)	20 (1)	12 (8)	42 (3)	6 (4)
C(2)	81 (4)	140 (7)	22 (1)	52 (9)	41 (3)	10 (5)
C(3)	80 (4)	163 (8)	23 (1)	12 (9)	49 (4)	5 (5)
C(4)	80 (4)	127 (7)	22 (1)	14 (8)	39 (3)	15 (5)
C(5)	82 (4)	117 (7)	27 (1)	39 (8)	40 (4)	9 (5)
C(6)	71 (3)	139 (7)	23 (1)	46 (8)	43 (3)	−2 (5)
C(7)	80 (4)	127 (7)	24 (1)	25 (8)	46 (3)	11 (5)
C(8)	116 (5)	157 (8)	30 (1)	79 (11)	64 (4)	18 (6)
C(9)	122 (5)	195 (10)	48 (2)	126 (13)	89 (6)	28 (8)
C(10)	91 (5)	212 (11)	41 (2)	62 (12)	37 (5)	56 (8)
C(11)	107 (5)	199 (10)	31 (2)	10 (12)	31 (5)	25 (7)
C(12)	93 (4)	174 (9)	25 (1)	16 (10)	39 (4)	−4 (6)
C(13)	71 (3)	128 (7)	21 (1)	18 (8)	30 (3)	10 (5)
C(14)	91 (4)	129 (7)	30 (1)	16 (9)	55 (4)	23 (5)
C(15)	73 (4)	156 (8)	28 (1)	20 (9)	34 (4)	13 (5)
C(16)	68 (3)	172 (8)	22 (1)	−3 (9)	29 (3)	8 (5)
C(17)	81 (4)	196 (10)	32 (1)	−8 (10)	38 (4)	46 (6)
C(18)	86 (4)	166 (9)	30 (1)	34 (10)	43 (4)	40 (6)
C(19)	84 (4)	120 (7)	21 (1)	0 (8)	42 (3)	−12 (5)
N(20)	76 (3)	145 (6)	26 (1)	34 (7)	47 (3)	18 (4)
O(21)	90 (3)	154 (5)	32 (1)	69 (6)	67 (3)	45 (4)
N(22)	120 (4)	181 (8)	29 (1)	127 (10)	83 (4)	39 (5)
O(23)	188 (5)	153 (7)	70 (2)	83 (10)	166 (6)	28 (6)
O(24)	110 (4)	341 (10)	26 (1)	203 (10)	27 (3)	10 (5)
N(25)	115 (4)	153 (7)	28 (1)	16 (9)	58 (4)	19 (5)
O(26)	137 (4)	231 (8)	43 (1)	11 (9)	104 (4)	51 (5)
O(27)	151 (4)	205 (8)	46 (1)	85 (10)	85 (4)	85 (6)
N(28)	92 (4)	124 (6)	39 (1)	56 (8)	73 (4)	23 (5)
O(29)	73 (3)	204 (7)	46 (1)	55 (7)	51 (3)	16 (5)
O(30)	144 (4)	230 (8)	36 (1)	34 (9)	98 (4)	−15 (5)
$\times 10^5$						
Br	931 (5)	2557 (13)	443 (2)	180 (13)	744 (5)	420 (8)

[a] Anisotropic temperature factors are expressed in the form, $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. Estimated standard deviations are given in parentheses.

The C(2)–C(1)–C(6) angle in the picryl ring is much less (116.4 (4)°) than 120° and is close to the angles at a carbon bearing either a nitrogen or oxygen substituent between two ortho nitro groups in 2,3,4,6-tetranitroaniline,[12] in 2,2-diphenyl-1-picrylhydrazyl free radical,[13] and in 2,4,6-trinitrophenetole.[14] The angle is, however, considerably larger than those found at the carbon-bearing oxygen substituents in picrate salts (111.1–111.5°)[15] or in Meisenheimer complexes (107–110°).[16]

The oxygen atom O(21) and the nitrogen atoms of the two ortho nitro groups (N(22) and N(28)) deviate by −0.095, 0.144, and −0.134 Å, respectively, from the best plane through the picryl ring, while the nitrogen atom of the para nitro group lies in this plane. The extent and disposition of these deviations almost certainly result from the steric overcrowding in that region of the molecule. The best plane through the group of atoms C(1), C(7), C(13), C(19), N(20), and O(21)

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(13) D. E. Williams, *J. Amer. Chem. Soc.*, **89**, 4280 (1967).

(14) C. M. Gramaccioli, R. Destro, and M. Simonetta, *Acta Crystallogr., Sect. B*, **24**, 129 (1968).

(15) K. Maartmann-Moe, *ibid., Sect. B*, **25**, 1452 (1969).

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Table IV

Bond lengths, Å,[a] in the molecule of **1c** with estimated standard deviations			
C(1)–C(2)	1.397 (6)	C(13)–C(18)	1.392 (6)
C(2)–C(3)	1.383 (6)	C(13)–C(19)	1.484 (6)
C(3)–C(4)	1.371 (6)	C(7)–C(19)	1.484 (6)
C(4)–C(5)	1.374 (7)	C(19)–N(20)	1.291 (6)
C(5)–C(6)	1.386 (6)	N(20)–O(21)	1.441 (5)
C(1)–C(6)	1.391 (6)	C(1)–O(21)	1.349 (5)
C(7)–C(8)	1.390 (7)	N(22)–O(23)	1.216 (6)
C(8)–C(9)	1.385 (8)	N(22)–O(24)	1.218 (7)
C(9)–C(10)	1.382 (9)	C(2)–N(22)	1.467 (6)
C(10)–C(11)	1.387 (8)	C(4)–N(25)	1.480 (6)
C(11)–C(12)	1.373 (8)	N(25)–O(26)	1.214 (7)
C(7)–C(12)	1.386 (7)	N(25)–O(27)	1.217 (6)
C(13)–C(14)	1.389 (6)	C(6)–N(28)	1.473 (6)
C(14)–C(15)	1.375 (7)	N(28)–O(29)	1.219 (6)
C(15)–C(16)	1.384 (7)	N(28)–O(30)	1.217 (6)
C(16)–C(17)	1.357 (7)	C(16)–Br	1.894 (4)
C(17)–C(18)	1.386 (7)		
Bond angles, deg,[b] with standard deviations in parentheses			
C(2)–C(1)–C(6)	116.4 (4)	C(14)–C(13)–C(19)	121.6 (4)
C(2)–C(1)–O(21)	114.5 (3)	C(18)–C(13)–C(19)	119.9 (3)
C(6)–C(1)–O(21)	129.0 (4)	C(13)–C(14)–C(15)	121.5 (4)
C(1)–C(2)–C(3)	123.2 (4)	C(14)–C(15)–C(16)	118.4 (3)
C(1)–C(2)–N(22)	119.1 (3)	C(15)–C(16)–C(17)	121.7 (5)
C(3)–C(2)–N(22)	117.7 (4)	C(15)–C(16)–Br	119.0 (2)
C(2)–C(3)–C(4)	117.1 (4)	C(17)–C(16)–Br	119.3 (2)
C(3)–C(4)–C(5)	123.0 (4)	C(16)–C(17)–C(18)	119.7 (3)
C(3)–C(4)–N(25)	118.5 (3)	C(13)–C(18)–C(17)	120.2 (3)
C(5)–C(4)–N(25)	118.5 (3)	C(7)–C(19)–C(13)	119.5 (2)
C(4)–C(5)–C(6)	118.1 (3)	C(7)–C(19)–N(20)	125.1 (3)
C(1)–C(6)–C(5)	122.1 (4)	C(13)–C(19)–N(20)	115.3 (4)
C(1)–C(6)–N(28)	122.1 (4)	C(19)–N(20)–O(21)	108.1 (3)
C(5)–C(6)–N(28)	115.8 (4)	C(1)–O(21)–N(20)	112.9 (2)
C(8)–C(7)–C(12)	118.9 (3)	C(2)–N(22)–O(23)	117.1 (5)
C(8)–C(7)–C(19)	120.8 (4)	C(2)–N(22)–O(24)	117.7 (4)
C(12)–C(7)–C(19)	120.3 (3)	O(23)–N(22)–O(24)	125.0 (3)
C(7)–C(8)–C(9)	119.5 (3)	C(4)–N(25)–O(26)	117.6 (4)
C(8)–C(9)–C(10)	121.5 (6)	C(4)–N(25)–O(27)	117.3 (4)
C(9)–C(10)–C(11)	118.5 (4)	O(26)–N(25)–O(27)	125.1 (3)
C(10)–C(11)–C(12)	120.4 (4)	C(6)–N(28)–O(29)	117.0 (4)
C(7)–C(12)–C(11)	121.2 (4)	C(6)–N(28)–O(30)	117.3 (4)
C(14)–C(13)–C(18)	118.5 (3)	O(29)–N(28)–O(30)	125.6 (3)

[a] The C–H lengths range from 0.76 to 1.12 Å with a typical standard deviation of 0.07 Å. [b] The C–C–H angles range from 112 to 130° with a typical standard deviation of 3°.

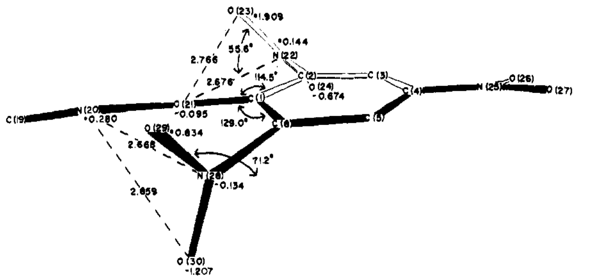

Figure 3. Diagram showing certain dimensions in or around the picryl ring in **1c**. The distances with positive and negative signs refer to the deviations of the atoms from the best plane through the six carbon atoms of the picryl ring (plane A in Table V).

makes an angle of 18.2° with the plane of the picryl ring, while the nitro groups attached to C(2), C(4), and C(6) make angles of 55.6, 13.0, and 71.2°, respectively, with the plane of the picryl ring. Another feature of the geometry of the nitro groups is the substantial deviation (0.081 and 0.089 Å) of the attached carbon atom in the picryl ring (C(2) and C(6)) from the planes defined by the three atoms in each ortho nitro group; in contrast, C(4) lies only 0.016 Å from the plane of N(25), O(26), and O(27).

A further effect of the intramolecular overcrowding of the substituents on the picryl ring is to be seen in the values for the exocyclic angles at C(1): C(2)–C(1)–O(21) is 114.5 (3) while C(6)–C(1)–O(21) is 129.0° (4). The combined effect of these bond angle distortions at C(1), the out-of-plane bending of the substituents at C(6), C(1), and C(2), and the large rotations of the ortho nitro groups relative to the picryl ring is to minimize steric interaction between, on the one hand, N(20) and the nitro group (N(28)–O(29)–O(30)), and on the other, O(21) and the nitro group (N(22)–O(23)–O(24)) (Figure 3). The N(20)---N(28) and N(20)---O(30) contacts are 2.668 (5) and 2.859 (5) Å, while the O(21)---N(22) and O(21)---O(23) contacts are 2.676 (6) and 2.766 (6) Å. The dipolar nature of the nitro group may result in the interactions in this region of the molecule being a delicate balance between attractive and repulsive forces, as may be the case in several other structures, *e.g.*, 2,3,4,6-tetranitroaniline,[12] *o*-nitrobenzaldehyde,[17] *o*-nitrobenzoic acid,[18] and *o*-nitroperoxybenzoic acid.[19]

The C(1)–O(21) length of 1.349 (5) Å is shorter than those found in Meisenheimer complexes (1.40–1.42 Å),[16] but agrees well with the phenolic length found in salicylic acid.[20] The C(19)–N(20) bond length (1.291 (6) Å) agrees well with the values found in other oximes,[21] and seems to confirm the early prediction by Cox and Jeffrey[22] that the C–N bond in oxime *O*-ethers should be a pure double bond. The phenyl rings C(7)–C(12) and C(13)–C(18) make angles of 60.5 and 18.6° with the best plane through the significantly nonplanar group of atoms, C(7), C(13), C(19), N(20), and O(21). The large angle of rotation of the C(7)–C(12) ring out of the central plane is probably due to steric influences from the syn oxygen atom, as comparably large angles of twist for the phenyl rings syn to oxygen are observed in the two molecules of **1b**. The bromine-containing phenyl ring is also bent out of the central plane.

Some important intermolecular contacts in the crystal of **1c** are listed in Table VI, while Figure 4 is a stereoscopic view of the packing looking along the c^* direction. The oxygen atoms of the N(25)–O(26)–O(27) nitro group are in close contact with two of the hydrogen atoms of the C(7)–C(12) phenyl ring in the molecule at $x, 1\tfrac{1}{2} - y, -\tfrac{1}{2} + z$. There are fairly close contacts between the N(25)–O(26)–O(27) and N(28)–O(29)–O(30) nitro groups in the basic molecule and the N(22)–O(23)–O(24) nitro group in the molecule at $x, 1 + y, z$. C(19) and N(20) in the basic molecule are 3.21 and 3.22 Å from O(29) in the molecule at $1 - x, 1 - y, 1 - z$, while H(8) is 2.94 Å from O(29). Although the C(13)–C(18) phenyl ring appears to be stacked parallel and above

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Table V. Distances (Å) from Various Best Planes in the Molecule **1c**[a]

Atom	A	B	C	D	E	F	G	H	I
C(1)	**−0.006**						**−0.046**	−0.097	−0.082
C(2)	**0.027**	0.081							
C(3)	**−0.021**								
C(4)	**−0.006**		0.016				−0.216	−0.312	−0.294
C(5)	**0.027**								
C(6)	**−0.018**			0.089					
C(7)					**0.003**		**−0.007**	**0.009**	0.045
C(8)					**0.000**				
C(9)					**−0.005**				
C(10)					**0.003**		−0.106	−0.066	0.075
C(11)					**0.004**				
C(12)					**−0.005**				
C(13)						**−0.009**	**−0.044**	**−0.031**	−0.099
C(14)						**0.005**			
C(15)						**0.008**			
C(16)						**−0.013**	−0.285	−0.249	−0.404
C(17)						**0.010**			
C(18)						**0.005**			
C(19)					0.032	−0.084	**0.018**	**0.020**	**0.000**
N(20)	0.280						**0.050**	**0.030**	**0.000**
O(21)	−0.095						**0.007**	**−0.021**	**0.000**
N(22)	0.144	**0.000**							
O(23)	1.090	**0.000**							
O(24)	−0.674	**0.000**							
N(25)	−0.001		**0.000**				−0.304	−0.425	−0.405
O(26)	−0.233		**0.000**						
O(27)	0.248		**0.000**						
N(28)	−0.134			**0.000**					
O(29)	0.834			**0.000**					
O(30)	−1.207			**0.000**					
Br							−0.502	−0.450	−0.665
χ^2 [b]	74.3				1.6	14.6	293.3	125.5	
P[c]	≪0.005				~0.5	~0.005	≪0.005	≪0.005	

[a] Distances of atoms included in the best plane calculations are given in bold type. The equations of the following planes relative to the orthogonal axes *a*, *b*, and *c** are: plane A, $-0.2495X - 0.5126Y - 0.8216Z + 12.6641 = 0$; plane E, $0.6163X + 0.7847Y - 0.0672Z - 3.2194 = 0$; plane F, $-0.1523X - 0.4528Y - 0.8785Z + 12.7655 = 0$; plane G, $0.0054X - 0.6790Y - 0.7341Z + 11.3530 = 0$. [b] χ^2 values calculated on the basis of standard deviations obtained by multiplying those from the least-squares results by 1.3. [c] Probability that deviations describe a normal distribution.

Table VI. Intermolecular Contacts (Å) in the Crystal of **1c**[a]

O(26)---H(12)^{I}	3.15	C(19)---O(29)^{IV}	3.21
O(27)---H(12)^{I}	3.14	N(20)---O(29)^{IV}	3.22
O(26)---H(11)^{I}	2.85	O(29)---H(8)^{IV}	2.94
O(24)---Br^{II}	3.57	N(22)---O(24)^{V}	2.88
C(5)---H(8)^{III}	3.13	O(24)---O(24)^{V}	2.93
N(25)---O(23)^{III}	3.31	O(24)---O(23)^{V}	3.06
O(27)---O(23)^{III}	3.25	O(24)---H(3)^{V}	2.76
O(30)---H(18)^{III}	3.03	O(23)---H(3)^{V}	2.69

[a] I corresponds to x, $1^1/_2 - y$, $-^1/_2 + z$; II corresponds to $1 + x$, y, z; III corresponds to x, $1 + y$, z; IV corresponds to $1 - x$, $1 - y$, $1 - z$; V corresponds to $2 - x$, $1 - y$, $1 - z$.

Table VII. Important Intermolecular Contacts (Å) in **1b**[a]

C(1)---C(15′)	3.50	C(4′)---N(20)^{II}	3.28
C(1)---C(16′)	3.47	C(5′)---C(14)^{II}	3.47
C(5)---O(26)^{I}	3.10	O(26′)---C(1)^{II}	3.09
C(5)---O(30′)^{I}	3.35	O(27′)---O(30)^{II}	3.37
O(30)---C(5′)^{I}	2.90	O(29)---N(22)^{III}	3.04
O(30)---N(28′)^{I}	3.08	O(29)---O(23)^{III}	3.07
O(29′)---N(25)^{I}	3.19	O(29)---O(24)^{III}	3.17
C(3′)---N(20)^{II}	3.10	Br---O(24)^{IV}	3.30

[a] I refers to $1 - x$, $^1/_2 + y$, $^1/_2 - z$; II refers to $1 + x$, y, z; III refers to x, $1 + y$, z; IV refers to $1 - x$, $-y$, $1 - z$.

the picryl ring in the molecule at $1 - x$, $1 - y$, $1 - z$, the shortest C---C contact is 3.49 Å between C(16) and C(4). The contacts that imply the strongest intermolecular interaction involve the N(22)–O(23)–O(24) nitro group in the basic molecule and the centrosymmetrically related group at $2 - x$, $1 - y$, $1 - z$; the N(22)---O(24)^{V} contact of 2.88 Å is marginally shorter than the sum of the appropriate van der Waals radii[23] (2.90 Å).

The large number of intermolecular contacts involving atoms of the nitro groups may indicate that a portion of the large rotations of the nitro groups out of the plane of the picryl ring may result from intermolecular forces. Trotter[24,25] has presented evidence that rotations of aromatic nitro groups out of the planes of the attached phenyl rings beyond 35–40° should be sensitive to packing or intermolecular effects, as there will be little loss of conjugation beyond this point.

There are no short intermolecular contacts between the groups that migrate in the Beckmann rearrangement. Whereas the intramolecular C(19)---O(21) distance is 2.213 (5) Å (sum of the appropriate van der Waals radii is 3.1 Å), there are no corresponding intermolecular contacts less than 4 Å.

The conformations of the two crystallographically equivalent molecules of **1b** are quite similar (Figure 5). In the "unprimed" molecule, the picryl ring, the C(7)–C(12) phenyl ring, and the C(13)–C(18) phenyl ring make angles of 43°45′, 62°7′, and 22°50′ with the best plane through C(1), O(21), N(20), C(19), C(7), and C(13). In the "primed" molecule, the corresponding angles are 28°29′, 76°50′, and 17°41′. Thus, in both **1b** and

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(23) L. Pauling in "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1962, pp 257–264.

(24) J. Trotter, *Acta Crystallogr.*, **12**, 237 (1959).

(25) J. Trotter, *ibid.*, **12**, 232 (1959).

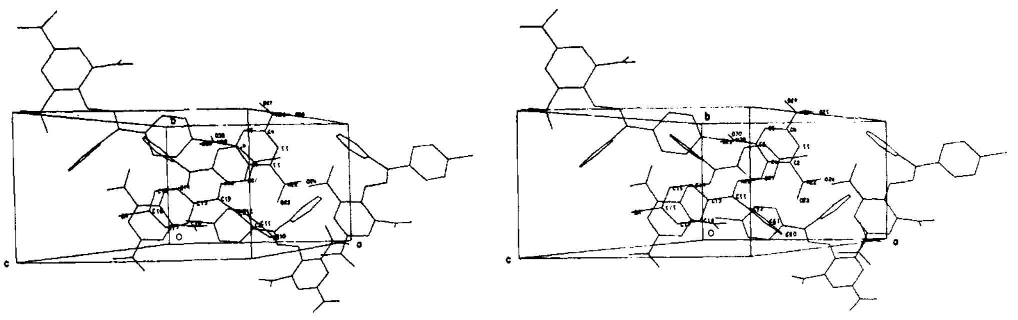

Figure 4. Stereoscopic view of the packing of **1c** looking along *c**.

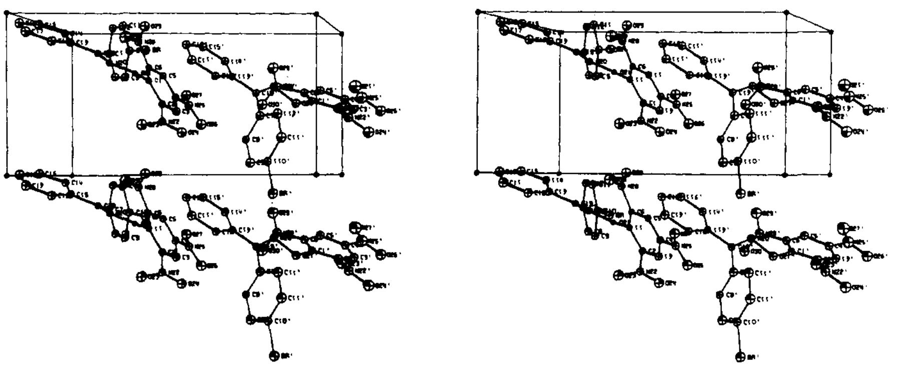

Figure 5. Stereoscopic view of four molecules of **1b** looking along the *c** direction. The "box" shown corresponds to one-quarter of the unit cell in the *c* direction.

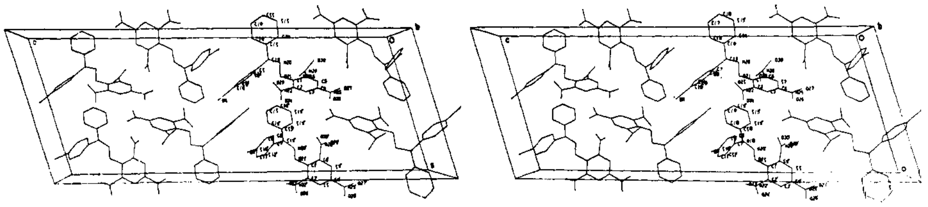

Figure 6. Stereoscopic view of the unit cell of **1b** looking down the *b* axis. The molecules with the atom numbers correspond to those whose coordinates are given in Table I.

1c, the phenyl ring syn to the picryl ring has the largest rotation out of the central plane. In the unprimed molecule of **1b** the nitro groups at C(2), C(4), and C(6) are rotated out of the plane of the picryl ring by 39.6, 7.0, and 53.6°, respectively, while in the primed molecule the corresponding angles are 30.2, 16.7, and 58.6°. As in the anti isomer, N(20) and N(28) are displaced substantially in opposite directions from the plane of the picryl ring. There are great similarities in the conformations and dispositions of the groups attached to the picryl ring in the two molecules of **1b** and in the molecule of **1c**.

Some intermolecular contacts in the crystal of **1b** are given in Table VII. Figure 6 is a stereoscopic view of the packing in **1b** looking down the *b* axis. The O(30)---C(5′)$^{\mathrm{I}}$ contact of 2.90 Å is very short but probably does not represent a hydrogen bond as O(30) lies 2.02 Å out of the plane of the picryl ring containing C(5′)$^{\mathrm{I}}$; O(30) is also quite close to N(28′) in the same asymmetric unit. The relatively short C(3′)---N(20)$^{\mathrm{II}}$ contact of 3.10 Å cannot represent a hydrogen bond because of the geometry. The Br---O(24)$^{\mathrm{IV}}$ distance of 3.30 Å is 0.15 Å less than the sum of the van der Waals radii.[23]

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