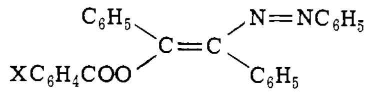
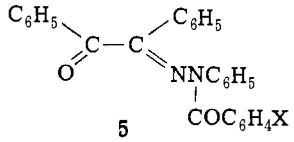


4



5

bond of 4 must be trans and that the rate-determining step of the rearrangement is the isomerization of 4 from the trans to the cis isomer. The demonstration that **2b** has the trans configuration has similar implications with respect to the measurements reported earlier[4a] of the rate of rearrangement of **2a** to **3a**. The stability of **2a** to illumination was surprising. A sample allowed to sit in the daylight in a sealed Pyrex tube showed no change after 4 months; no evidence of isomerization to a cis isomer was obtained.

Acknowledgment. We wish to thank Ms. Nina Thayer for her assistance in the preparation of this paper.

Crystal and Molecular Structures of Diphenyl Triketone *sym-N*-Benzoylphenylhydrazone and Diphenyl Triketone *sym-N*-Benzoyl-*p*-bromophenylhydrazone[1,2]

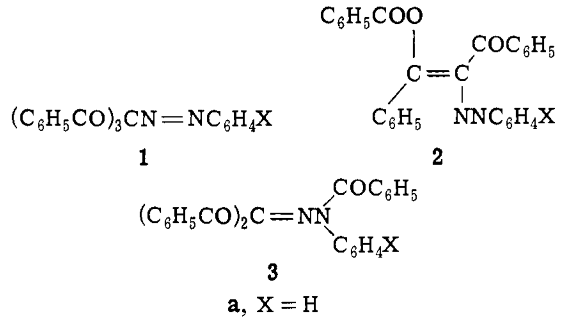
Daniel B. Pendergrass, Jr., Iain C. Paul,*[3] and David Y. Curtin*

Contribution from the Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

Received February 2, 1972

Abstract: The crystal structures of diphenyl triketone *sym-N*-benzoylphenylhydrazone (**3a**) and diphenyl triketone *sym-N*-benzoyl-*p*-bromophenylhydrazone (**3b**) have been determined. The molecules **3a** and **3b** are, respectively, the final products of the solid state rearrangement of phenylazotribenzoylmethane (**1a**) and its *p*-bromophenylazo analog **1b**. The crystals of **3a** and **3b** are isostructural. The crystals of **3a** are orthorhombic with a = 35.750 (16), b = 11.090 (5), and c = 5.735 (4) Å; there are four molecules of $C_{28}H_{20}N_2O_3$ in the space group $Pna2_1$. The structure has been refined to an R factor of 0.083 on 1321 nonzero reflections measured by counter methods. The molecule of **3b** crystallizes in the orthorhombic system, with a = 35.876 (11), b = 11.417 (3), and c = 5.765 (4) Å; there are four molecules of $C_{28}H_{19}N_2O_3Br$ in the space group $Pna2_1$. The structure has been refined to an R factor of 0.066 on 2005 nonzero reflections collected by counter methods. The structural results on these two compounds help correct some errors and clarify some ambiguities in the existing literature. The surprisingly small effect of the introduction of a bromine atom in **3b** upon the packing of these molecules is discussed.

The molecules of phenylazotribenzoylmethane (**1a**) and its *p*-bromo derivative **1b** have been shown to undergo thermal rearrangement reactions in the solid state to the red enol benzoates **2a** and **2b** and the white *N*-benzoylhydrazones **3a** and **3b**.[4] In the case of the bromo derivative **1b**, the crystal form of the *N*-benzoylhydrazone **3b** produced in the solid state rearrangement differs from that obtained by crystallization of **3b** from methanol.[4a] This paper reports the crystal structure of the benzoylhydrazone **3a** and of the form of **3b** obtained by crystallization.



1

2

3

a, X = H

b, X = Br

Experimental Section

X-Ray Analysis of Diphenyl Triketone *sym*-Benzoylphenylhydrazone (3a). Diphenyl triketone *sym*-benzoylphenylhydrazone (**3a**) crystallizes from methylene chloride as very fine white needles (mp 204–205°).

Crystal Data: $C_{28}H_{20}N_2O_3$; M = 432.46; orthorhombic; a = 35.750 (16), b = 11.090 (5), c = 5.735 (4) Å; V = 2274 Å^3; D_m = 1.23 (by flotation in aqueous $ZnCl_2$); Z = 4, D_c = 1.26; $F(000)$ = 904, μ = 6.8 cm^{-1} (Cu Kα, λ = 1.54178 Å); systematic absences, $0kl$, when $k + 1 = 2n + 1$, $h0l$, when $h = 2n + 1$; space group $Pna2_1$. (The systematic absences are also consistent with the space group $Pnam$, but the presence of only four molecules in the unit cell would require that the molecule have a center cf symmetry or a mirror plane.)

The determination of the cell parameters and the measurement of the intensity data were carried out as described previously.[4c] The best crystal which, however, still did not give a very extensive diffraction pattern was a very fine needle (0.05 × 0.05 × 0.25 mm) and was mounted about the c axis (dimension 0.25 mm). Of the

---

[1] Taken in part from the Ph.D. Thesis of Daniel B. Pendergrass, Jr., submitted to the University of Illinois, 1971.

[2] We are indebted to the National Science Foundation and to the Advanced Research Projects Agency of the Department of Defense (Contract HC 15-67-C-0221) for partial support of this work.

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

[4] (a) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 88, 4637 (1966); (b) D. Y. Curtin, S. R. Byrn, and D. B. Pendergrass, Jr., *J. Org. Chem.*, **34**, 3345 (1969); (c) D. B. Pendergrass, Jr., D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 8722 (1972).

Table I. Atomic Coordinates of **3a** and **3b** in Fractions of the Unit Cell Edges with Estimated Standard Deviations in Parentheses

	3a			3b		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	0.0642 (4)	1.0330 (14)	0.888[a]	0.0762 (2)	0.9601 (7)	0.887 (2)
C(2)	0.0618 (5)	0.9730 (15)	0.681 (4)	0.0697 (3)	0.9104 (8)	0.673 (2)
C(3)	0.0876 (3)	0.8850 (11)	0.614 (3)	0.0948 (3)	0.8248 (8)	0.595 (2)
C(4)	0.1188 (3)	0.8703 (10)	0.759 (2)	0.1249 (2)	0.7992 (6)	0.733 (2)
C(5)	0.1227 (4)	0.9327 (12)	0.958 (3)	0.1322 (3)	0.8529 (8)	0.943 (2)
C(6)	0.0964 (4)	1.0188 (11)	1.023 (3)	0.1067 (3)	0.9364 (8)	1.020 (3)
C(7)	0.1101 (2)	0.6098 (9)	0.781 (3)	0.1142 (2)	0.5482 (7)	0.773 (2)
C(8)	0.0826 (3)	0.6627 (10)	0.950 (2)	0.0892 (2)	0.6067 (7)	0.952 (2)
C(9)	0.1070 (3)	0.4751 (10)	0.754 (3)	0.1079 (3)	0.4160 (7)	0.755 (2)
C(10)	0.1762 (3)	0.8121 (10)	0.572 (2)	0.1807 (2)	0.7380 (7)	0.513 (2)
C(11)	0.0418 (3)	0.6688 (9)	0.895 (3)	0.0501 (2)	0.6305 (7)	0.898 (2)
C(12)	0.0160 (3)	0.7154 (11)	1.054 (3)	0.0276 (2)	0.6862 (8)	1.062 (2)
C(13)	−0.0210 (3)	0.7172 (13)	1.005 (3)	−0.0098 (3)	0.7074 (8)	1.015 (2)
C(14)	−0.0337 (4)	0.6738 (13)	0.792 (3)	−0.0247 (3)	0.6732 (9)	0.808 (2)
C(15)	−0.0091 (3)	0.6298 (12)	0.631 (3)	−0.0026 (3)	0.6177 (9)	0.630 (2)
C(16)	0.0291 (3)	0.6263 (11)	0.680 (3)	0.0346 (3)	0.5989 (7)	0.683 (2)
C(17)	0.1296 (3)	0.4045 (9)	0.578 (3)	0.1282 (3)	0.3416 (8)	0.593 (2)
C(18)	0.1448 (3)	0.4513 (12)	0.378 (3)	0.1444 (3)	0.3754 (9)	0.387 (2)
C(19)	0.1648 (5)	0.3788 (17)	0.231 (3)	0.1631 (4)	0.2987 (12)	0.243 (3)
C(20)	0.1676 (5)	0.2576 (21)	0.294 (5)	0.1637 (4)	0.1790 (11)	0.317 (3)
C(21)	0.1533 (5)	0.2097 (16)	0.487 (5)	0.1474 (4)	0.1430 (10)	0.521 (4)
C(22)	0.1341 (4)	0.2855 (14)	0.630 (4)	0.1298 (3)	0.2206 (9)	0.657 (3)
C(23)	0.2056 (3)	0.7226 (12)	0.518 (3)	0.2091 (2)	0.6455 (9)	0.464 (2)
C(24)	0.2158 (3)	0.6365 (15)	0.683 (4)	0.2197 (3)	0.5643 (10)	0.637 (3)
C(25)	0.2437 (4)	0.5564 (13)	0.640 (5)	0.2492 (4)	0.4859 (16)	0.592 (4)
C(26)	0.2620 (5)	0.5642 (21)	0.429 (6)	0.2662 (5)	0.4926 (20)	0.379 (4)
C(27)	0.2532 (5)	0.6437 (24)	0.263 (5)	0.2558 (5)	0.5717 (21)	0.213 (3)
C(28)	0.2250 (3)	0.7270 (14)	0.308 (3)	0.2276 (4)	0.6537 (17)	0.260 (3)
N(1)	0.1446 (2)	0.7787 (7)	0.688 (2)	0.1504 (2)	0.7064 (6)	0.655 (1)
N(2)	0.1374 (2)	0.6603 (7)	0.680 (2)	0.1414 (2)	0.5891 (5)	0.655 (1)
O(1)	0.0943 (2)	0.6910 (7)	1.144 (2)	0.1031 (2)	0.6260 (6)	1.139 (1)
O(2)	0.0861 (2)	0.4233 (7)	0.888 (3)	0.0853 (2)	0.3774 (5)	0.892 (2)
O(3)	0.1805 (2)	0.9165 (7)	0.506 (2)	0.1837 (2)	0.8384 (5)	0.453 (2)
Br				0.04108 (4)	1.07028 (9)	1.0000[a]
H(1)	0.048 (4)	1.088 (12)	0.93 (3)			
H(2)	0.044 (4)	0.982 (15)	0.61 (3)	0.050 (2)	0.932 (7)	0.56 (2)
H(3)	0.086 (4)	0.848 (12)	0.42 (3)	0.092 (3)	0.798 (9)	0.37 (2)
H(5)	0.145 (3)	0.921 (11)	1.07 (3)	0.152 (3)	0.824 (9)	1.11 (2)
H(6)	0.100 (2)	1.060 (7)	1.18 (2)	0.109 (2)	0.963 (7)	1.21 (2)
H(12)	0.030 (3)	0.736 (11)	1.16 (3)	0.040 (3)	0.697 (8)	1.28 (2)
H(13)	−0.037 (2)	0.745 (7)	1.14 (2)	−0.023 (3)	0.736 (10)	1.17 (3)
H(14)	−0.061 (3)	0.664 (11)	0.75 (3)	−0.052 (2)	0.676 (8)	0.82 (2)
H(15)	−0.015 (3)	0.598 (9)	0.51 (2)	−0.015 (2)	0.605 (7)	0.48 (2)
H(16)	0.045 (3)	0.600 (10)	0.56 (3)	0.050 (2)	0.557 (6)	0.54 (2)
H(18)	0.143 (3)	0.563 (9)	0.35 (2)	0.144 (2)	0.451 (8)	0.35 (2)
H(19)	0.171 (4)	0.410 (12)	0.09 (3)	0.170 (3)	0.326 (11)	−0.02 (2)
H(20)	0.180 (4)	0.228 (16)	0.18 (4)	0.175 (3)	0.128 (10)	0.28 (2)
H(21)	0.154 (3)	0.144 (9)	0.52 (2)	0.149 (4)	0.061 (12)	0.72 (3)
H(22)	0.122 (3)	0.250 (10)	0.71 (2)	0.119 (2)	0.207 (6)	0.81 (2)
H(24)	0.205 (3)	0.647 (11)	0.84 (3)	0.202 (3)	0.572 (11)	0.82 (3)
H(25)	0.251 (2)	0.488 (7)	0.76 (2)	0.255 (4)	0.415 (11)	0.84 (3)
H(26)	0.278 (3)	0.516 (9)	0.43 (2)	0.288 (4)	0.443 (13)	0.28 (3)
H(27)	0.263 (5)	0.699 (16)	0.10 (3)	0.269 (3)	0.578 (11)	0.07 (3)
H(28)	0.215 (3)	0.810 (11)	0.15 (3)	0.222 (4)	0.707 (12)	0.21 (3)

[a] Held constant to determine the origin in the *z* direction.

2309 independent reflections measured, 1321 were considered significantly above zero at the 1σ level.[5]

The structure was solved by the symbolic addition procedure[6] using the SIGMA2-CONVERGE-FASTAN series of programs.[7] Convergence mapping[7] based on the 378 reflections with normalized structure amplitudes, $|E|$, greater than 1.22 suggested the choice of 1 3 0, 19 2 0, and 5 2 1 for the origin-determining reflections and 12 3 1, 17 1 0, 2 5 0, and 3 2 0 for the starting set. In addition, the reflection 2 6 0 was assigned the phase 0° after application of the Σ_1 formula.[8] Following tangent formula refinement, the phase set with the highest absolute figure of merit[7] was used to calculate an E map from which the positions of the 33 nonhydrogen atoms were immediately apparent. Four cycles of least-squares refinement varying positional and isotropic thermal parameters reduced R to 0.146 and R_2 ($[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$) to 0.129. Unit weights were given to all nonzero reflections and the quantity minimized was $\Sigma w||F_o| - |F_c||^2$. Refinement of the positions of the hydrogen atoms with isotropic thermal parameters and of the nonhydrogen atoms with anisotropic thermal parameters required that the model be refined in two parts. The first part contained C(1–7), C(9), C(10), C(17–28), N(1), N(2), O(2), O(3), and attached hydrogen atoms; the second consisted of C(1–8), C(10–16), C(23–28), N(1), N(2), O(1), O(3), and attached hydrogen atoms. Final values of R of 0.083 and R_2 of 0.080 were obtained after four cycles of refinement on each fragment. The largest peak found in a difference map computed after refinement had a height of 0.1 e/Å^3. The calculated values for the unobserved reflections did not reveal any anomalies. The final coordinates and thermal parameters are listed in Tables I and II.

---

(5) A program, EDABS, written by E. C. Bissell in this laboratory was used to process the data.

(6) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(7) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

(8) H. Hauptman and J. Karle, "Solution of the Phase Problem. 1. The Centro-symmetric Crystal," ACA Monograph No. 3, American Crystallographic Association, 1953.

Table II. Final Thermal Parameters for the Atoms in **3a**[a,b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0014 (2)	0.010 (2)	0.044 (8)	0.0018 (4)	0.003 (1)	−0.001 (3)
C(2)	0.0014 (2)	0.012 (2)	0.045 (8)	0.0021 (5)	0.002 (1)	0.005 (3)
C(3)	0.0011 (1)	0.006 (1)	0.053 (9)	0.0001 (3)	−0.001 (1)	0.001 (3)
C(4)	0.0006 (1)	0.007 (1)	0.024 (4)	−0.0001 (3)	0.001 (1)	−0.002 (2)
C(5)	0.0013 (2)	0.009 (1)	0.042 (7)	0.0009 (4)	−0.001 (1)	−0.001 (3)
C(6)	0.0017 (2)	0.009 (1)	0.017 (5)	0.0005 (4)	0.001 (1)	−0.005 (2)
C(7)	0.0005 (1)	0.006 (1)	0.029 (5)	−0.0002 (3)	−0.001 (1)	−0.001 (2)
C(8)	0.0006 (1)	0.009 (1)	0.016 (4)	−0.0004 (3)	0.000 (1)	0.003 (2)
C(9)	0.0006 (1)	0.006 (1)	0.052 (7)	−0.0001 (3)	0.000 (1)	0.002 (3)
C(10)	0.0007 (1)	0.007 (1)	0.025 (5)	−0.0003 (3)	0.000 (1)	0.002 (2)
C(11)	0.0007 (1)	0.005 (1)	0.043 (6)	0.0002 (2)	−0.002 (1)	−0.001 (2)
C(12)	0.0009 (1)	0.007 (1)	0.038 (6)	0.0002 (3)	0.001 (1)	−0.004 (3)
C(13)	0.0006 (1)	0.015 (2)	0.028 (5)	0.0007 (4)	0.000 (1)	−0.008 (3)
C(14)	0.0008 (1)	0.010 (1)	0.047 (7)	0.0002 (4)	0.000 (1)	0.001 (3)
C(15)	0.0009 (1)	0.012 (2)	0.029 (6)	−0.0004 (4)	0.000 (1)	−0.009 (3)
C(16)	0.0006 (1)	0.007 (1)	0.023 (4)	0.0002 (3)	0.002 (1)	0.001 (2)
C(17)	0.0005 (1)	0.006 (1)	0.051 (7)	−0.0005 (3)	−0.002 (1)	−0.004 (2)
C(18)	0.0009 (1)	0.009 (1)	0.037 (6)	0.0002 (4)	−0.001 (1)	−0.005 (3)
C(19)	0.0015 (2)	0.012 (2)	0.034 (7)	0.0015 (5)	−0.001 (1)	−0.009 (3)
C(20)	0.0011 (2)	0.016 (3)	0.062 (10)	0.0011 (6)	−0.003 (1)	−0.010 (5)
C(21)	0.0019 (2)	0.006 (2)	0.077 (13)	0.0008 (5)	−0.005 (2)	0.000 (4)
C(22)	0.0010 (2)	0.008 (2)	0.077 (11)	−0.0003 (4)	0.001 (1)	−0.002 (4)
C(23)	0.0004 (1)	0.011 (1)	0.054 (7)	−0.0004 (3)	0.000 (1)	−0.001 (3)
C(24)	0.0006 (1)	0.014 (2)	0.059 (8)	0.0009 (4)	−0.002 (1)	−0.009 (4)
C(25)	0.0012 (2)	0.009 (2)	0.071 (10)	0.0008 (4)	0.001 (1)	0.000 (4)
C(26)	0.0007 (2)	0.020 (3)	0.101 (17)	0.0010 (6)	−0.003 (1)	−0.014 (7)
C(27)	0.0010 (2)	0.021 (3)	0.074 (12)	−0.0011 (7)	0.002 (1)	−0.004 (6)
C(28)	0.0008 (1)	0.013 (2)	0.051 (8)	0.0005 (4)	0.000 (1)	0.000 (3)
N(1)	0.0007 (1)	0.007 (1)	0.036 (4)	−0.0002 (3)	0.001 (1)	−0.001 (2)
N(2)	0.0007 (1)	0.005 (1)	0.032 (4)	0.0003 (2)	−0.001 (1)	−0.003 (2)
O(1)	0.0009 (1)	0.011 (1)	0.035 (4)	0.0003 (2)	0.000 (1)	0.000 (2)
O(2)	0.0009 (1)	0.008 (1)	0.068 (1)	−0.0008 (2)	0.001 (1)	0.007 (2)
O(3)	0.0011 (1)	0.008 (1)	0.065 (6)	−0.0003 (2)	0.002 (1)	0.004 (2)

	B_θ		B_θ		B_θ		B_θ
H(1)	9 (4)	H(12)	8 (4)	H(18)	4 (3)	H(24)	4 (4)
H(2)	9 (6)	H(13)	1 (2)	H(19)	17 (4)	H(25)	1 (2)
H(3)	7 (4)	H(14)	9 (4)	H(20)	7 (6)	H(26)	3 (3)
H(5)	7 (4)	H(15)	1 (2)	H(21)	2 (3)	H(27)	9 (7)
H(6)	1 (2)	H(16)	3 (3)	H(22)	2 (3)	H(28)	7 (4)

[a] Anisotropic thermal parameters expressed as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters as $\exp[-(B_\theta \sin^2 \theta/\lambda^2)]$.

X-Ray Analysis of Diphenyl Triketone *sym*-Benzoyl-*p*-bromophenylhydrazone (3b). Diphenyl triketone *sym*-benzoyl-*p*-bromophenylhydrazone (**3b**) crystallizes from methylene chloride as very fine white needles (mp 228–229°).

Crystal Data: $C_{28}H_{19}N_2O_3Br$; $M = 511.37$; orthorhombic; $a = 35.876\ (11)$, $b = 11.417\ (3)$, $c = 5.765\ (4)$ Å; $V = 2362$ Å^3; $D_m = 1.40$ (by flotation in aqueous $ZnCl_2$); $Z = 4$; $D_c = 1.44$; $F(000) = 1040$; $\mu = 28.9$ cm^{-1} (Cu Kα, $\lambda = 1.54178$ Å); systematic absences, $0kl$, when $k + 1 = 2n + 1$, $h0l$, when $h = 2n + 1$; space group, $Pna2_1$.

The best crystal that could be found for data collection was a fine needle with dimensions *ca.* 0.1 × 0.1 × 0.3 mm, with the *c* axis being the needle axis. Intensity data were collected as described previously.[4a] With the threshold count being taken as 0.1 times total background count or 50 counts, whichever was greater, 2005 of the 2232 independent reflections measured were considered to be significantly above background. No absorption corrections were applied; the maximum and minimum transmission coefficients were estimated to be 0.75 and 0.67.

The structure was solved by Patterson heavy atom methods despite some difficulties arising from pseudo-symmetry which prevented assignment of many atomic positions in the initial Fourier map. Two cycles of full-matrix least-squares refinement, varying positional and isotropic thermal parameters for all the nonhydrogen atoms, reduced R to 0.185 and R_2 to 0.174. Introduction of anisotropic thermal parameters required that the model be refined in two segments, the first of which contained Br, N(1) N(2), O(3), C(1–6), C(10), and C(23–28). The second fragment consisted of Br, O(1), O(2), C(7–9), and C(11–22). Four cycles of refinement for each fragment varying positional and anisotropic thermal parameters gave values for R of 0.075 and R_2 of 0.076. The positions of the hydrogen atoms were estimated using standard criteria. Refinement of the hydrogen atom parameters was achieved by a division of the molecule into two rather different segments, one consisting of the atoms Br, N(1), N(2), C(1–9), C(11–22), O(1), and O(2) with any attached hydrogen atoms, while the other was made up of Br, N(1), N(2), C(1–7), C(9), C(10), C(17–28), O(2) and O(3) and attached hydrogen atoms. Two cycles of refinement gave values for R of 0.066 and for R_2 of 0.064 on the 2005 nonzero reflections. The scattering curves used in both analyses were taken from ref 9, that for bromine being corrected for the real and imaginary components of anomalous dispersion.[10] The positional and thermal parameters for the atoms of **3b** are listed in Tables I and III. The final values of h, k, l, $|F_o|$, F_c, and α_c for both **3a** and **3b** will be published in the microfilm edition of the journal.[11]

Results and Discussion

Some of the bond lengths and angles found in the molecules of **3a** and **3b** are listed in Table IV. High

---

(9) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 201–209.

(10) D. H. Templeton in ref 9, pp 213–216.

(11) Tables of observed and calculated structure factors for 3a and 3b, the C–C length and C–C–C angles in the phenyl rings, some details of best planes and angles between planes for 3a and 3b, and the intermolecular contacts in both crystals will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-8730. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table III. Final Thermal Parameters for the Atoms in **3b**[a,b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.00154 (1)	0.0089 (1)	0.070 (1)	0.0014 (1)	0.0035 (1)	0.001 (1)
C(1)	0.00077 (8)	0.0052 (6)	0.037 (4)	0.0002 (2)	0.0009 (5)	−0.001 (1)
C(2)	0.00101 (9)	0.0070 (8)	0.028 (4)	0.0002 (2)	−0.0002 (5)	0.000 (2)
C(3)	0.00087 (8)	0.0063 (7)	0.032 (4)	−0.0002 (2)	−0.0002 (5)	0.002 (1)
C(4)	0.00068 (7)	0.0045 (6)	0.032 (4)	−0.0002 (2)	−0.0003 (4)	0.000 (1)
C(5)	0.00089 (8)	0.0067 (6)	0.044 (5)	−0.0003 (2)	−0.0007 (5)	−0.003 ()2
C(6)	0.00126 (10)	0.0064 (7)	0.041 (5)	−0.0005 (2)	0.0003 (7)	−0.005 (2)
C(7)	0.00070 (7)	0.0056 (6)	0.024 (3)	0.0001 (2)	0.0001 (4)	0.002 (1)
C(8)	0.00076 (7)	0.0059 (6)	0.026 (4)	−0.0002 (2)	−0.0005 (4)	0.002 (1)
C(9)	0.00082 (8)	0.0060 (7)	0.045 (5)	0.0001 (2)	−0.0009 (5)	0.001 (2)
C(10)	0.00076 (7)	0.0081 (7)	0.030 (4)	−0.0005 (2)	0.0001 (5)	−0.004 (2)
C(11)	0.00075 (7)	0.0050 (6)	0.031 (4)	−0.0001 (2)	−0.0004 (4)	0.000 (1)
C(12)	0.00087 (8)	0.0078 (7)	0.022 (4)	0.0001 (2)	0.0007 (4)	−0.001 (1)
C(13)	0.00099 (9)	0.0091 (8)	0.026 (4)	0.0005 (2)	−0.0001 (5)	0.001 (2)
C(14)	0.00090 (9)	0.0082 (9)	0.047 (5)	0.0000 (2)	−0.0001 (6)	0.007 (2)
C(15)	0.00096 (9)	0.0073 (8)	0.031 (4)	0.0001 (2)	−0.0006 (5)	0.001 (2)
C(16)	0.00091 (8)	0.0059 (7)	0.024 (3)	0.0002 (2)	0.0004 (4)	−0.001 (1)
C(17)	0.00082 (8)	0.0059 (7)	0.038 (4)	0.0001 (2)	−0.0002 (5)	−0.002 (1)
C(18)	0.00119 (11)	0.0075 (9)	0.038 (5)	0.0003 (3)	−0.0007 (6)	−0.005 (2)
C(19)	0.00137 (13)	0.0118 (13)	0.034 (5)	0.0002 (3)	−0.0001 (7)	−0.006 (2)
C(20)	0.00126 (13)	0.0094 (11)	0.072 (9)	0.0009 (3)	−0.0010 (9)	−0.016 (3)
C(21)	0.00132 (13)	0.0093 (10)	0.066 (7)	0.0007 (3)	−0.0024 (9)	−0.007 (3)
C(22)	0.00114 (11)	0.0067 (8)	0.048 (5)	0.0000 (2)	0.0008 (7)	−0.001 (2)
C(23)	0.00062 (7)	0.0103 (9)	0.036 (4)	−0.0001 (2)	−0.0003 (5)	−0.004 (2)
C(24)	0.00086 (10)	0.0113 (10)	0.069 (7)	0.0007 (3)	−0.0008 (7)	−0.002 (3)
C(25)	0.00123 (15)	0.0166 (17)	0.077 (10)	0.0018 (4)	−0.0009 (10)	−0.013 (4)
C(26)	0.00117 (16)	0.0230 (26)	0.086 (12)	0.0016 (5)	−0.0029 (12)	−0.019 (5)
C(27)	0.00134 (16)	0.0308 (32)	0.050 (7)	0.0012 (6)	0.0032 (9)	−0.006 (4)
C(28)	0.00113 (13)	0.0183 (20)	0.051 (7)	0.0003 (4)	0.0028 (8)	−0.002 (3)
N(1)	0.00074 (6)	0.0055 (5)	0.028 (3)	0.0000 (1)	0.0007 (4)	0.000 (1)
N(2)	0.00076 (6)	0.0047 (5)	0.031 (3)	0.0001 (1)	−0.0003 (4)	−0.001 (1)
O(1)	0.00089 (6)	0.0085 (6)	0.030 (2)	0.0000 (1)	−0.0016 (3)	0.000 (1)
O(2)	0.00107 (6)	0.0068 (5)	0.056 (4)	0.0001 (2)	0.0030 (4)	0.002 (1)
O(3)	0.00103 (6)	0.0075 (5)	0.059 (4)	−0.0005 (1)	0.0020 (4)	0.004 (1)

	B_θ		B_θ		B_θ		B_θ
H(2)	4 (2)	H(12)	4 (3)	H(18)	5 (2)	H(24)	5 (4)
H(3)	8 (3)	H(13)	7 (4)	H(19)	16 (4)	H(25)	9 (4)
H(5)	7 (3)	H(14)	6 (2)	H(20)	8 (3)	H(26)	15 (5)
H(6)	4 (2)	H(15)	4 (2)	H(21)	10 (5)	H(27)	11 (4)
		H(16)	5 (2)	H(22)	2 (2)	H(28)	10 (5)

[a] Anisotropic thermal parameters expressed as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters as $\exp[-(B_\theta \sin^2 \theta/\lambda^2)]$.

Table IV. Some Bond Lengths (Å) and Bond Angles (deg) in **3a** and **3b**[a]

	3a	**3b**		**3a**	**3b**
C(4)-N(1)	1.43 (1)	1.47 (1)	C(8)-C(11)	1.49 (2)	1.46 (1)
N(1)-N(2)	1.34 (1)	1.38 (1)	C(8)-O(1)	1.23 (2)	1.21 (1)
N(1)-C(10)	1.36 (2)	1.41 (1)	C(7)-C(9)	1.51 (2)	1.53 (1)
C(10)-C(23)	1.48 (2)	1.49 (1)	C(9)-C(17)	1.51 (2)	1.46 (1)
C(10)-O(3)	1.23 (1)	1.20 (1)	C(9)-O(2)	1.22 (2)	1.22 (1)
C(7)-N(12)	1.27 (1)	1.28 (1)	C(1)-Br		1.90 (1)
C(7)-C(8)	1.50 (2)	1.52 (1)			
N(1)-C(4)-C(3)	115 (1)	118 (1)	C(23)-C(10)-O(3)	119 (1)	124 (1)
N(1)-C(4)-C(5)	123 (1)	118 (1)	N(1)-N(2)-C(7)	124 (1)	122 (1)
C(8)-C(11)-C(12)	122 (1)	120 (1)	N(2)-C(7)-C(8)	129 (1)	131 (1)
C(8)-C(11)-C(16)	119 (1)	121 (1)	N(2)-C(7)-C(9)	117 (1)	116 (1)
C(9)-C(17)-C(18)	125 (1)	127 (1)	C(8)-C(7)-C(9)	114 (1)	113 (1)
C(9)-C(17)-C(22)	115 (1)	115 (1)	C(7)-C(8)-C(11)	122 (1)	120 (1)
C(10)-C(23)-C(24)	120 (1)	121 (1)	C(7)-C(8)-O(1)	118 (1)	116 (1)
C(10)-C(23)-C(28)	121 (1)	117 (1)	C(11)-C(8)-O(1)	120 (1)	124 (1)
C(4)-N(1)-N(2)	126 (1)	124 (1)	C(7)-C(9)-C(17)	123 (1)	123 (1)
C(4)-N(1)-C(10)	119 (1)	118 (1)	C(7)-C(9)-O(2)	117 (1)	114 (1)
N(2)-N(1)-C(10)	114 (1)	115 (1)	C(17)-C(9)-O(2)	120 (1)	123 (1)
N(1)-C(10)-C(23)	121 (1)	117 (1)	C(2)-C(1)-Br		118 (1)
N(1)-C(10)-O(3)	121 (1)	119 (1)	C(6)-C(1)-Br		118 (1)

[a] Bond lengths and angles involving the carbon atoms of the phenyl rings have been deposited.[11]

thermal motion in the crystal and the shortage of data limit the accuracy of the results in the case of **3a**. The average C–C(phenyl) length in **3a** is 1.377 Å with a root mean square deviation of 0.022 Å, a value which is slightly *lower* than the average standard deviation obtained from the least-squares results. Systematic

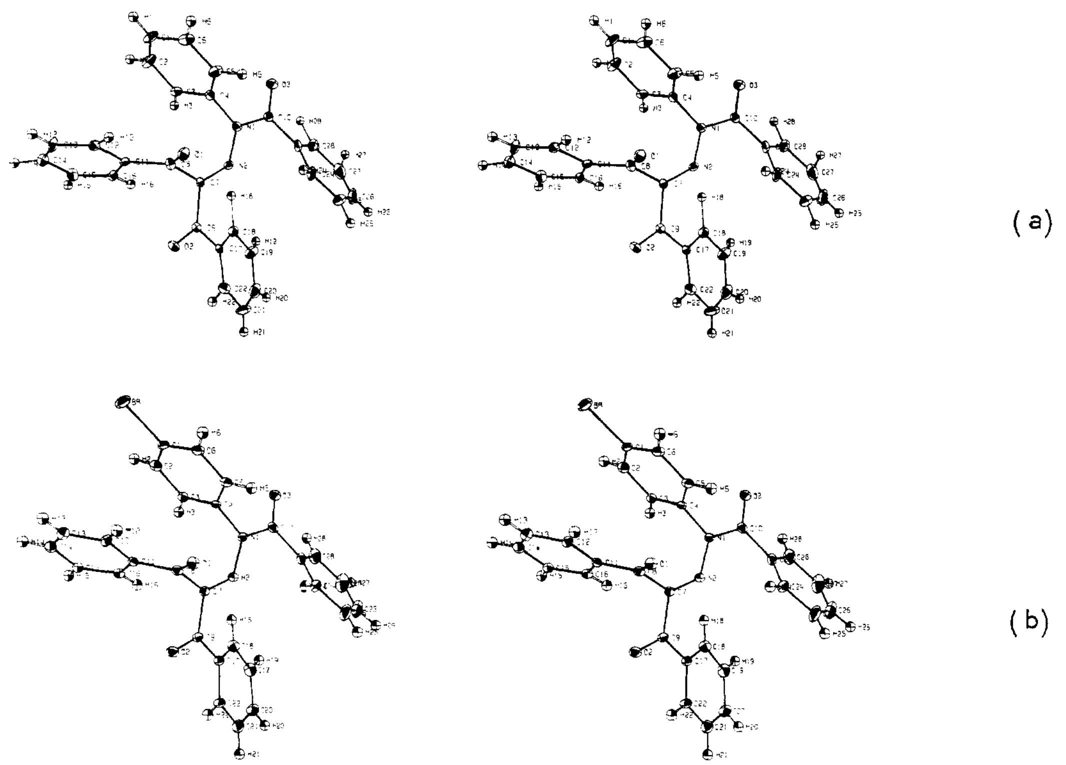


Figure 1. Stereoscopic views of single molecules of (a) **3a** and (b) **3b** looking along the *c* axis.

Table V. Summary of Bond Lengths Involving Nitrogen Atoms in **3a**, **3b**, and Certain Related Structures

	N—N	N=N	N—C- (aliphatic)	N—C- (aromatic)	N—C(vinyl)	N—C(amide)	N=C
1a[a]		1.233 (4)	1.479 (4)	1.443 (5)			
2b[a]		1.279 (8)[b]		1.448 (10)	1.401 (10)		
3a	1.34 (1)			1.43 (1)		1.36 (2)	1.27 (1)
3b	1.38 (1)			1.47 (1)		1.41 (1)	1.28 (1)
4[c]	1.33 (2)			1.36 (2)[d] 1.42 (2)		1.30 (2)	1.27 (2)
5[e]	1.36 (3)			1.39 (3)[d] 1.42 (3)		1.34 (3)	1.29 (3)
Range	1.33-1.38	1.23-1.28	1.48	1.42-1.47 1.36-1.39[d]	1.40	1.30-1.41	1.27-1.29

[a] Reference 4c. [b] This N=N double bond is part of a conjugated C=CN=N grouping. [c] Reference 12. [d] This is the length of a C—N bond between a nitrogen atom and the carbon of phenyl ring with the *o*-nitro group. [e] Reference 15.

errors are more serious in the case of **3b**, where the average C-C(phenyl) length was 1.390 Å with a root mean square deviation of 0.025 Å, while the standard deviations from the least-squares results range from 0.013 to 0.032 Å. The high thermal motion and the neglect of absorption corrections are probably major limitations on the accuracy of the analysis of **3b**. Stereoscopic drawings of single molecules of **3a** and **3b** are given in Figure 1. Packing diagrams for **3a** and **3b** are contained in Figure 2, and it is seen that the compounds are isostructural. The very close similarity in the conformations of **3a** and **3b** can be judged by the fact that the dihedral angles[11] between several pairs of planes in the two molecules agree within 7°.

A comparison of the bond distances involving nitrogen atoms in structures **3a** and **3b** with those in structurally related compounds is of particular interest. The crystal structure of 2,3-diketobutyranilide 2-(2-nitro-4-chlorophenylhydrazone) (**4**) has been reported.[12] Curiously both in the title of this paper and elsewhere[13] this compound has been designated as the phenylazo isomer although the hydrazone formula **4** is convincingly established by the dimensions obtained from the X-ray structure determination.[12] The hydrazone structure has also been shown to be the more stable tautomer by spectral studies in solution and in the solid state of 2,3-diketobutyranilide 2-phenylhydrazone.[14] The crystal structure of the hydrazone **5** has also been determined.[15] In the title of this paper the compound is named as the tautomeric azo compound, and the azo structure was the only one explicitly presented in the paper. However, it was recognized by the author that the X-ray data were not consistent with the azo structure written; they are, in fact, indicative of tautomer **5**. The bond lengths for the nitrogen–nitrogen and nitrogen–carbon bonds in this series of rather closely related hydrazones

---

[12] H.-C. Mez, *Ber. Bunsenges. Phys. Chem.*, **72**, 389 (1968).

[13] O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Vol. I, International Union of Crystallography, 1970, p 133.

[14] Y. Yagi, *Bull. Chem. Soc. Jap.*, **36**, 487, 492 (1963).

[15] C. J. Brown, *J. Chem. Soc. A*, 405 (1967).

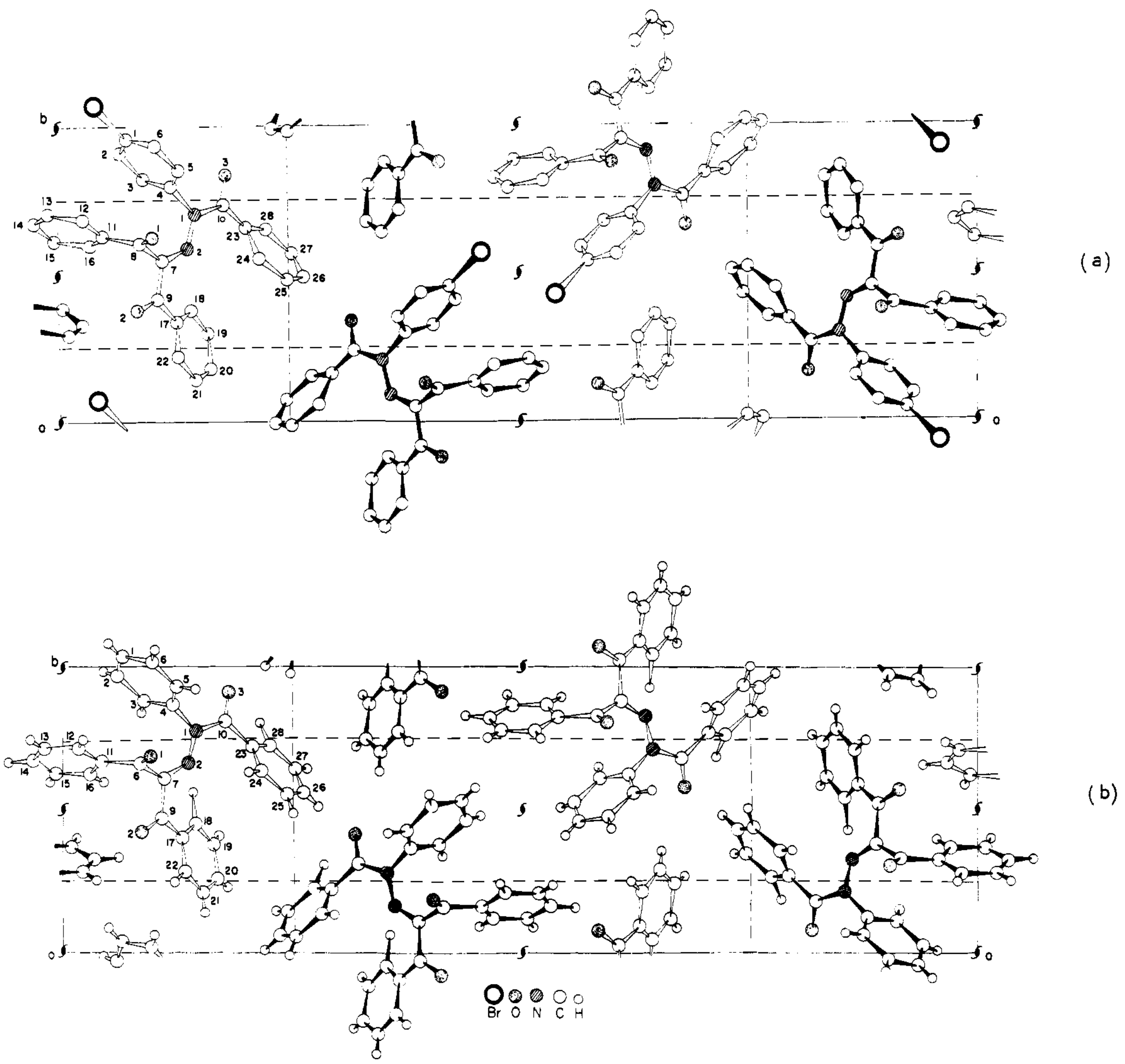
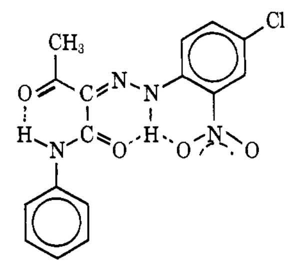


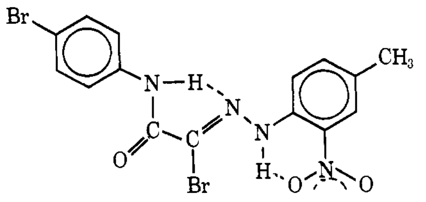
Figure 2. (a) Packing diagram of **3a** looking along the *c* axis; (b) packing diagram of **3b** looking along the *c* axis.

are shown in Table V together with a summary of the ranges observed.

It will be noted that the lengths of the N(1)–N(2) bonds [1.34 (1) and 1.38 (1) Å in **3a** and **3b**, respectively] agree with the value of 1.380 (14) Å for the single bond distance between the sp^2 hybridized nitrogen atoms in benzal azine.[16] While the N(1)–C(10) bond is slightly longer than is sometimes found in amides,[17] it clearly has considerable double bond character, and N–C-(amide) lengths of 1.352 (6), 1.354 (3), and 1.366 (3) Å have been reported in *N*-phenylurethane,[18] acetanilide,[19] and *N*,*N*-diphenylacetamide,[20] respectively. Correspondingly, the C(7)–N(2) lengths of 1.27 (1) and 1.28 (1) Å are indicative of double bonds, as are found in oxime *O*-picryl ethers.[21]



4



5

With these data as background it is useful to consider the structure of the coupling product of *p*-nitrophenyldiazonium ion and β-napththol which, on the basis of an X-ray crystal structure determination,[22] has been designated as the azo structure **6**. Comparison of the N–N distance of 1.345 (7) Å with the ranges in Table V and also the short C=O distance of 1.259

---

(16) U. C. Sinha, *Acta Crystallogr., Sect. B*, **26**, 889 (1970); compare J. Marignan, J. L. Galigné, and J. Falgueirettes, *ibid.*, 28, 93 (1972).

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 281.

(18) P. Ganis, G. Avitabile, S. Migdal, and M. Goodman, *J. Amer. Chem. Soc.*, **93**, 3328 (1971).

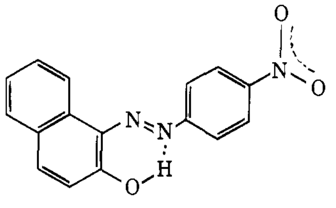
(19) C. J. Brown, *Acta Crystallogr.*, **21**, 442 (1966).

(20) W. R. Krigbaum, R.-J. Roe, and J. D. Woods, *Acta Crystallogr., Sect. B*, **24**, 1304 (1968).

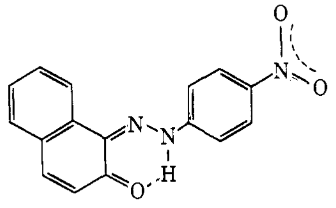
(21) J. D. McCullough, Jr., I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **94**, 883 (1972).

(22) C. T. Grainger and J. F. McConnell, *Acta Crystallogr., Sect. B*, **25**, 1962 (1969).

(10) Å which is nearer the C=O distance of 1.23 Å for the carbonyl group[23] than the C–O distance (1.35 Å) found in phenols[24] casts some doubt on this assignment. The C–O and adjacent C–N [1.331 (10) Å] distances in the coupling product agree well with those found in *o*-benzoquinone oxime structures.[25,26] Taken as a whole then the X-ray structural data seem to be more consistent with the hydrazone structure **7** than with the azo structure **6**. It may be noted that in solution such substances have been shown to exist as equilibrium mixtures of azo compound and hydrazone. With electronegative groups such as *p*-nitro in the phenylazo ring the hydrazone form is greatly favored, however.[27]

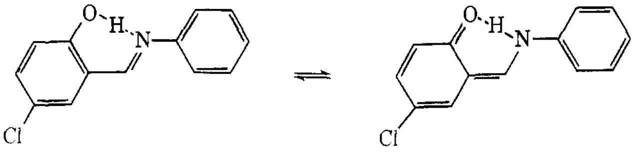


6



7

Another area to which the present results are relevant is the thermochromism exhibited in the solid state by anils of *o*-hydroxybenzaldehyde.[28] X-Ray structure analyses[29] have been carried out on both the room temperature (red) and low (90°K) temperature (yellow) forms of *N*-5-chlorosalicylideneaniline.



8 **9**

The phenomenon of thermochromism in these compounds can reasonably be explained on the basis of a tautomerism between **8** and **9**. However, the results of both X-ray analyses were in good agrement with each other and, on the basis of a comparison with the present results, are in each case consistent with structure **8**. The X-ray analysis of the room temperature form contained no evidence for a hydrogen atom attached to nitrogen. As was suggested previously,[28] it seems likely that tautomer **9**, although present as a solid solution in **8** in a large enough concentration to affect the visible spectrum, was not present in sufficient quantity to affect the X-ray results.

The *N*-benzoylhydrazones are of unusual interest not only because they are among the first hydrazones for which crystal structures have been obtained but also because they are examples of N-trisubstituted amides. The amide groups [C(23), C(10), O(3), N(1), C(4), and N(2)] in **3a** and **3b** are significantly nonplanar [deviations of −0.21 to 0.14 and −0.22 to 0.15 Å, respectively],[11] a property that seems to be fairly characteristic of amides substituted at nitrogen. Unlike the cases of *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride[18] and *N*,*N*-diphenylacetamide,[20] where the nonplanarity is mainly due to a torsion about the C–N bond, the nonplanarity is the result of a substantial pyramidal distortion at nitrogen. In **3a**, the C(23)–C(10)–N(1)–N(2) torsion angle is −20.4°, while the O(3)–C(10)–N(1)–C(4) angle is −7.9°; in **3b** the corresponding torsion angles are −26.2 and −2.8°. N(1) deviates by 0.101 and 0.133 Å from the plane defined by its three bonded neighbors in **3a** and **3b**, respectively. These distortions presumably arise from overcrowding between N(2) and H(24) and are rather similar to those in 4-diethylcarbamoyl-1-cyclohexene-5-carboxylic acid[30] and in *N*,*N*′-diethyl-*N*,*N*′-diphenylurea.[31]

A survey of N-substituted amides whose structures have been determined[18,19,31,32] reveals a general trend to place the bulkier groups trans to each other around the partial double C–N bond. In this context, when a phenyl group can rotate to a near-orthogonal position with respect to the plane of the amide group, it is considered to be less bulky than a methyl or methylene group; *e.g.*, the conformation of *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride[18] has the ethyl group trans to the chlorine atom with the phenyl ring rotated 70° out of the plane of the amide group. This trend is observed in **3a** and **3b**, where the two phenyl groups are trans to each other. In cases where relief of overcrowding cannot readily be achieved by rotation of substituents, pyramidal distortion at nitrogen seems particularly significant.[30,31] In cases where there are bulky substituents on the ortho positions of phenyl rings attached either to the carbon or nitrogen atom of the amide groups, rotational isomers have been isolated.[33]

The packing in the two crystals is very similar (see Figure 2). Most of the intermolecular contacts[11] involve molecules related by a unit translation in the *z* direction, where O(1) in one molecule points into a crevice in the adjacent molecule created by the near-parallel arrangement of all the rings to form an approximate "H shaped" structure with the vertical sides of the H being elevated (see Figure 3). The shortest contact between individual atoms in such molecules involves N(2) and O(1) (3.46 Å in **3a** and 3.31 Å in **3b**). Most of the short (<3.7 Å) contacts between individual

---

(23) L. E. Sutton, *Chem. Soc. Spec. Publ.*, No. **11** (1965).

(24) H. Gillier-Pandraud, *Bull. Soc. Chim. Fr.*, 1988 (1967); P. Coppens and G. M. J. Schmidt, *Acta Crystallogr.*, **18**, 62, 654 (1965).

(25) C. Romers, *ibid.*, **17**, 1287 (1964).

(26) J. W. L. van Oijen and C. Romers, *ibid.*, **20**, 169 (1966).

(27) A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, *J. Chem. Soc. B*, 1308 (1968).

(28) M. D. Cohen, G. M. J. Schmidt, and S. Flavian, *J. Chem. Soc.*, 2041 (1964); M. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, *ibid.*, 2051, 2060 (1964); M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, **66**, 2442 (1962).

(29) J. Bregman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.*, 2068 (1964); J, Bregman, L. Leiserowitz, and K. Osaki, *ibid.*, 2086 (1964). Compare also G. Arcovito, M. Bonamico, A. Domenicano, and A. Vaciago, *J. Chem. Soc. B*, 733 (1969).

(30) C. Pedone, E. Benedetti, A. Immirzi, and G. Allegra, *J. Amer. Chem. Soc.*, **92**, 3549 (1970).

(31) P. Ganis, G. Avitabile, E. Benedetti, C. Pedone, and M. Goodman, *Proc. Nat. Acad. Sci. U. S.*, **67**, 426 (1970). The *z* coordinate of N(1) in this paper should be 0.3517 instead of 0.3317: M. Goodman and G. Avitabile, personal communication, 1971.

(32) B. F. Pedersen, *Acta Chem. Scand.*, **21**, 1415 (1967).

(33) T. H. Siddall III and R. H. Garner, *Can. J. Chem.*, **44**, 2387 (1966); H. A. Staab and D. Lauer, *Tetrahedron Lett.*, 4593 (1966); J. P. Chupp and J. F. Olin, *J. Org. Chem.*, **32**, 2297 (1967).

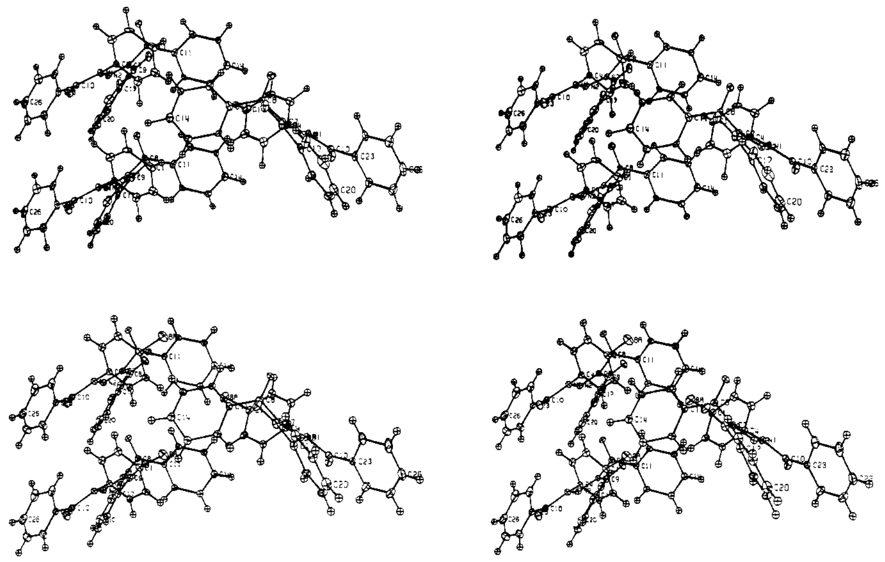


Figure 3. Stereoscopic views of relationship of molecules of (a) **3a** and (b) **3b** with the molecules related by the screw axis along the *c* axis. The structures are sufficiently similar that a pseudo-stereoscopic effect can be obtained by viewing this figure vertically and assuming the two packing diagrams to be the right and left images.

atoms are slightly greater in the case of **3a** than in the case of **3b**.[11] The departure of the phenyl rings from an exactly perpendicular arrangement with respect to the plane of the "H" allows a moderate amount of interleaving of phenyl rings between adjacent molecules in the *z* direction. The increase in contact between adjacent molecules in the *z* direction in **3b** when compared to **3a** is apparently partly balanced by a relaxation in contacts between C(14) and C(15) in the basic molecule and O(2) in the molecule at $-x$, $1 - y$, $-{}^1/_2 + z$ related by the screw axis. Thus, the C(14)---O(2) and C(15)---O(2) contacts are 3.17 and 3.14 Å in **3a** and 3.29 and 3.27 Å in **3b**. The orientations of the C–H bonds with respect to the oxygen atom, however, are inconsistent with C–H---O hydrogen bonding. The bromine atom is involved in a contact of 3.48 Å with C(14) in the molecule at $-x$, $2 - y$, ${}^1/_2 + z$.

The two compounds studied in this investigation are unusual in that the introduction of a bromine atom on the para position of one of the rings has not affected the major features of the packing. The situation found in **1a** and **1b**,[4c] where the molecular conformations are similar but the packing is quite different, is more typical. In the crystal of **3a**, the azo ring [C(1)–C(6)] is placed such that it points into the open space of the "H" of the molecule at $-x$, $2 - y$, ${}^1/_2 + z$ (related by the screw axis), with H(1) 3.40 Å from C(14) in that molecule (Figure 3a); H(1) is also 2.54 Å from H(13) and 3.40 Å from C (13) in the molecule at $-x$, $2 - y$, $-{}^1/_2 + z$. The direction of the C(1)–H(1) bond is such that its replacement with the much longer C(1)–Br bond can be accommodated by relatively minor adjustments in the positions of the molecules in the unit cell (Figure 3b); the resulting Br---C(14) contact is 3.48 Å. These arrangements of the molecules of **3a** and **3b** are shown in Figures 3a and 3b. The most significant change is a relative translation of the centers of the two molecules, related by the screw axis, in the *b* direction by about 1.3 Å (Figure 2). In addition, there are minor rotations of both the entire molecule and individual rigid groups. It is interesting to note that an early attempt to solve the structure of **3a** by using the coordinates of the carbon, nitrogen, and oxygen atoms from the refined model of **3b** was unsuccessful.

Acknowledgment. We thank Ms. Nina Thayer for assistance in the preparation of this manuscript.