

atoms outweighs the higher intrinsic affinity of Ln for single oxygen atoms, and that these complexes are totally inapplicable as shift reagents.

Experimental Section

The preparation of compounds used in this study is described

elsewhere.¹¹ Nmr spectra were recorded in frequency sweep or HR mode on a Varian HA-100 spectrometer fitted with a V-6040 variable temperature attachment, and are referenced to internal Me₄Si. Sample solutions were prepared either in carbon tetrachloride that had been stored over solid sodium hydroxide pellets or in commercial chloroform-*d*; each sample contained ~30 mg of complex per 0.3 cm³.

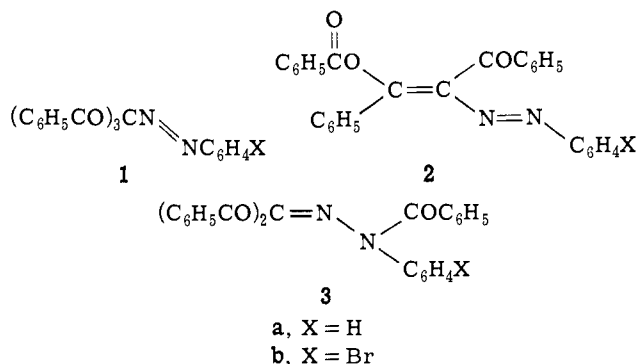
X-Ray Crystal Structure and Solid State Rearrangement of Phenylazotribenzoylmethane and the X-Ray Crystal Structure of α -*p*-Bromophenylazo- β -benzoyloxybenzalacetophenone^{1,2}

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

Contribution from the Department of Chemistry and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. Received February 2, 1972

Abstract: The crystal structure of the unsolvated form of phenylazotribenzoylmethane (**1a**), a molecule which undergoes a solid state rearrangement to α -phenylazo- β -benzoyloxybenzalacetophenone (**2a**) and to diphenyl triketone *sym*-benzoylphenylhydrazone (**3a**), has been determined by X-ray analysis. The yellow crystals of **1a** are monoclinic with $a = 13.054(5)$, $b = 10.352(5)$, $c = 16.560(10)$ Å; and $\beta = 90.78(1)^\circ$. The space group is $P2_1/c$ and there are four molecules of **1a** in the unit cell. The structure has been refined to an R factor of 0.047 on 2309 structure amplitudes measured on a diffractometer (Cu K α radiation). While the crystal structure of **1a** is quite different from that of *p*-bromophenylazotribenzoylmethane (**1b**), the molecular conformations are almost identical and appear to be influenced by intramolecular C=O...C=O (carbonyl) interactions. Features of the molecular conformation of **1a** are two C(carbonyl)...O(carbonyl) distances of 2.667(4) and 2.758(4) Å and two C(carbonyl)...N distances of 2.698(4) and 2.998(5) Å. Similar relative orientations of carbonyl groups are found in other di- (and poly-) ketones. There are no intermolecular distances in **1a** involving migrating centers less than 4.79 Å. The crystal structure of α -*p*-bromophenylazo- β -benzoyloxybenzalacetophenone (**2b**), one of the rearrangement products of **1b**, has also been determined. The red crystals of **2b** are triclinic, with $a = 10.031(3)$, $b = 6.309(3)$, $c = 19.387(6)$ Å; $\alpha = 96.78(3)$, $\beta = 103.78(2)$, and $\gamma = 90.54(3)^\circ$. There are two molecules in the unit cell and the space group is $P\bar{1}$. The structure has been refined to an R factor of 0.099 on 3510 nonzero structure amplitudes measured on a diffractometer (Cu K α). The stereochemistry about the N=N double bond is *trans*, while the migrating carbonyl group (to form **3b**) and the receiving *p*-bromophenylazo group are *trans* with respect to the C=C double bond. Kinetic studies of the rearrangement in the solid state of **1a** to a mixture of **2a** and **3a** showed, in the temperature range of 65–90°, an induction period followed by a rather good first-order fit throughout most of the reaction. Ratios of products **2a**:**3a** were independent of the origin of the starting material and of the fraction reacted but rather dependent on the temperature. The solid state rearrangements were slower than solution reactions by a factor of about 10². Chemically induced dynamic nuclear polarization and esr studies suggest that the rearrangements may be more complicated than might be inferred from the first-order kinetics observed in solution and in the solid state.

Phenylazotribenzoylmethane (**1a**) and a number of structurally related compounds have been shown to rearrange in good yield to a mixture of enol benzoate **2a** and hydrazone **3a** in nonpolar solvents at temperatures of 55° or higher.⁴ Such rearrangements have also been found to occur in the solid state;⁵ the solid state rearrangement of **1b** has been studied in some detail and the X-ray crystal structure reported.⁶ The unbrominated compound **1a** has been of particular in-



terest because it forms a crystalline hemietherate **1c** which loses the ether on standing to give **1a** in a different physical state.⁷ This paper reports the X-ray crystal structure and studies of the effect of the solid state on

(7) J. D. McCullough, Jr., D. Y. Curtin, L. L. Miller, I. C. Paul, and D. B. Pendergrass, Jr., *Mol. Cryst. Liquid Cryst.*, **11**, 407 (1970).

(1) Taken in part from the Ph.D. Thesis of D. 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 support of this work.

(3) Alfred P. Sloan Research Fellow, 1968–1970.

(4) (a) See D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4887, 4892 (1962), and earlier references cited therein; (b) D. Y. Curtin and L. L. Miller, *ibid.*, **89**, 637 (1967).

(5) D. Y. Curtin, S. R. Byrn, and D. B. Pendergrass, Jr., *J. Org. Chem.*, **34**, 3345 (1969).

(6) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **88**, 4637 (1966).

Table I. Cell Data of Compounds Studied

	1a ^a	1c ^b	1b ^c	2a	2b
	C ₂₈ H ₂₀ N ₂ O ₃	C ₂₈ H ₂₀ N ₂ O ₃ · 1/2 C ₆ H ₁₀ O	C ₂₈ H ₁₉ N ₂ O ₃ Br	C ₂₈ H ₂₀ N ₂ O ₃	C ₂₈ H ₁₉ N ₂ O ₃ Br
Crystal system		Monoclinic		Triclinic	
<i>a</i> , Å	13.054 (5)	10.07 (2)	9.84 (3)	17.576 (2)	10.031 (3)
<i>b</i> , Å	10.352 (5)	20.63 (4)	14.19 (4)	13.901 (2)	6.309 (3)
<i>c</i> , Å	16.560 (10)	13.54 (6)	18.56 (5)	10.447 (1)	19.387 (6)
α , deg	90.0	90.0	90.0	99.92 (2)	96.78 (4)
β , deg	90.78 (1)	115.7 (2)	111.8 (2)	113.62 (1)	103.78 (2)
γ , deg	90.0	90.0	90.0	90.22 (1)	90.54 (3)
<i>M</i>	432.46	469.52	511.37	432.46	511.37
<i>V</i> , Å ³	2238	2534	2404	2296	1182
<i>D_m</i> , g/cm ³	1.28		1.39	1.25	1.38
<i>D_c</i> , g/cm ³	1.28	1.23 ^d	1.41	1.25	1.43
<i>Z</i>	4	4	4	4	2
$\mu_{\text{Cu K}\alpha}$, cm ⁻¹	6.9	6.5	28.4	6.7	28.6
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1 or <i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$

^a Crystallized from xylene-hexane. ^b Hemihydrate of **1a**; see ref 7. ^c Reference 6. ^d Based on the assumption of a hemihydrate.

the rates and products of the rearrangement of the un-brominated azotriketone **1a**. The unknown stereochemistry of reaction products **2a,b** has been of interest in connection with the occurrence of **2** (as an intermediate) in the rearrangements of **1** to **3**. This stereochemical problem has been resolved by the determination of the X-ray crystal structure of **2b** which is also reported herein.

Experimental Section

X-Ray Structure Determination of Phenylazotribenzoylmethane (1a). Phenylazotribenzoylmethane (**1a**)⁴ crystallizes from a 1:1 mixture of xylene and hexane as yellow laths (mp 124°, at 40°/min mp 138°). Optical goniometry led to the tentative assignment of orientation of faces as follows. The most prominent face is (100), bounded on the sides by (110) and (1 $\bar{1}$ 0) and terminated on the ends by (10 $\bar{2}$).⁸ Crystal data for this and related compounds are presented in Table I. Cell dimensions for **1a**, **2a**, and **2b** were determined by a least-squares fit to the settings for the four angles on a Picker FACS-1 diffractometer (Cu K α radiation, $\lambda = 1.54051$ Å). The densities of **1a**, **2a**, and **2b** were measured by flotation in aqueous ZnCl₂.

Intensity data were collected on a crystal with dimensions ca. 0.1 × 0.2 × 0.3 mm on the diffractometer (Cu K α radiation). The reflections were measured by a scintillation counter, with attenuators being inserted when the count rate exceeded 10,000 counts sec⁻¹. All the symmetry-nonequivalent reflections in the 2 θ range 3–130° were measured by a moving crystal-moving counter technique, with a 2 θ scan rate of 2° min⁻¹. The base width of the scan was 2.0°, with a dispersion factor applied to allow for the α_1 - α_2 splitting; background counts at each limit of the scan were made for 10 sec. Of the 4213 measured reflections, 2309 were considered observed at the 2 σ level. No correction was made for absorption or extinction. Three standard reflections were recorded after every 50 measurements, and their intensities did not vary by more than $\pm 4\%$ during the period of irradiation.

The structure was solved by the symbolic addition procedure using the SIGMA2-CONVERGE-FASTAN series of programs.⁹ Two cycles of full-matrix least-squares refinement varying positional and isotropic thermal parameters for the 33 nonhydrogen atoms reduced *R* to 0.107 and *R*₂ to 0.103 where $R_2 = [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$. All reflections were given unit weight, and the

quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Introduction of anisotropic thermal parameters for the nonhydrogen atoms followed by further least-squares refinement reduced *R* to 0.081 and *R*₂ to 0.082. A difference map revealed the positions of all the hydrogen atoms. The addition of the hydrogen atoms, with isotropic thermal parameters, required that the model be refined in two segments, the first of which consisted of atoms C(1–9), C(11–22), N(1), N(2), O(1), O(2), and H(1–22). The second segment consisted of atoms C(7–28), O(1), O(2), O(3), and H(12–28). Two cycles of least-squares refinement on each fragment reduced *R* to 0.047 and *R*₂ to 0.045. The final fractional coordinates are listed in Table II.¹⁰ The largest peak on a difference map based on the complete model corresponds to an electron density of 0.25 e Å⁻³. The calculated amplitudes for the unobserved reflections did not have any anomalous values.

X-Ray Analysis of α -*p*-Bromophenylazo- β -benzoyloxybenzalacetophenone (2b). Enol benzoate **2b** was obtained in the form of red, needle-shaped crystals (mp 142–143°) by slow evaporation of a saturated acetone solution.

The procedures for collection of data on a crystal with dimensions 0.10 × 0.15 × 0.25 mm were as described previously with the exception that the scan rate was 1° min⁻¹. The intensities of the standard reflections were within $\pm 4\%$ of the initial values. Using the criteria that the threshold count be 0.1 × total background count or 50 counts, whichever is greater, a total of 3510 reflections out of a possible 4257 was considered to be significantly above zero. No absorption corrections were made; the maximum and minimum transmission coefficients were estimated to be 0.75 and 0.58.

The structure was solved by the heavy atom method based on bromine. Full-matrix least-squares refinement of the positional and anisotropic thermal parameters required that the model be refined in two segments with Br, N(1), N(2), O(1), C(1–8), and C(11–16) in one group and Br, O(2), O(3), C(9), C(10), and C(17–28) in the other. At the conclusion of this refinement, the *R* factor was 0.099 and *R*₂ was 0.103 on the 3896 nonzero reflections. No attempt was made to locate or include the hydrogen atoms in any calculations. The final positional parameters are given in Table II.¹⁰ The calculated structure amplitudes for the unobserved reflections did not indicate any anomalies. The scattering curves for Br, C, N, and O used in the two analyses were taken from "International Tables for X-ray Crystallography,"¹¹ with correction of the bromine scattering curve for anomalous dispersion,¹² while the curve for hydrogen was the one calculated by Stewart, *et al.*¹³

(8) The morphology can be compared with that of the *p*-bromo analog **1b** whose stereographic projection was reported⁹ and whose orientation has been confirmed by X-ray methods (J. D. McCullough, Jr., unpublished work) to be as follows: the most prominent faces, A and B (nomenclature employed in ref 6), are (0 $\bar{1}$ 1) and (0 $\bar{1}$ $\bar{1}$) terminated on the ends by E (100) and with a less well-developed face G. The major faces are the same ones reported earlier (P. Groth, "Chemische Kristallographie," Vol. 5, Verlag von W. Engelmann, Leipzig, 1919, p 355) for this compound although it was there formulated incorrectly.^{4a} The details of the crystal structures of **1a** and **1b** are consistent with these particular faces being well developed.

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

(10) The list of observed and calculated structure factors for **1a** and **2b**, the thermal parameters for **1a** and **2b**, the C–C (phenyl) lengths and C–C–C (phenyl) angles for both compounds, the torsion angles around several bonds in **1a** compared to those in **1b**, and some details of the C=O---C=O distances 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-72-8722. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche.

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

(12) D. H. Templeton in ref 11, pp 213–216.

Table II. Final Positional Parameters^a for the Atoms^b in **1a** and **2b**

1a				2b			
Atom	x	y	z	Atom	x	y	z
C(1)	1.0951 (3)	0.4689 (5)	0.1739 (3)	C(1)	1.2322 (8)	0.3231 (16)	0.9871 (4)
C(2)	1.0945 (3)	0.5796 (5)	0.2193 (3)	C(2)	1.2727 (9)	0.5173 (16)	0.9774 (5)
C(3)	1.0132 (2)	0.6660 (4)	0.2105 (2)	C(3)	1.1807 (8)	0.6368 (14)	0.9299 (4)
C(4)	0.9346 (2)	0.6396 (3)	0.1568 (2)	C(4)	1.0470 (7)	0.5440 (14)	0.8991 (4)
C(5)	0.9352 (3)	0.5283 (4)	0.1106 (3)	C(5)	1.0057 (8)	0.3457 (15)	0.9130 (4)
C(6)	1.0169 (4)	0.4436 (5)	0.1201 (3)	C(6)	1.0983 (9)	0.2259 (15)	0.9572 (4)
C(7)	0.6944 (2)	0.7906 (2)	0.1070 (1)	C(7)	0.7657 (7)	0.7248 (13)	0.7776 (4)
C(8)	0.6329 (2)	0.7789 (2)	0.1882 (1)	C(8)	0.8427 (7)	0.8814 (13)	0.7477 (4)
C(9)	0.6294 (2)	0.7570 (2)	0.0313 (1)	C(9)	0.6254 (7)	0.6875 (13)	0.7538 (3)
C(10)	0.7343 (2)	0.9319 (3)	0.1007 (2)	C(10)	0.5298 (7)	0.7400 (12)	0.6329 (3)
C(11)	0.5250 (2)	0.8234 (2)	0.1949 (1)	C(11)	0.9233 (7)	0.7961 (13)	0.6956 (4)
C(12)	0.4661 (2)	0.7610 (3)	0.2525 (2)	C(12)	1.0093 (9)	0.9368 (16)	0.6765 (5)
C(13)	0.3663 (2)	0.7970 (3)	0.2644 (2)	C(13)	1.0852 (9)	0.8598 (23)	0.6233 (6)
C(14)	0.3236 (2)	0.8979 (3)	0.2204 (2)	C(14)	1.0703 (9)	0.6446 (20)	0.5951 (6)
C(15)	0.3821 (2)	0.9608 (3)	0.1634 (2)	C(15)	0.9849 (9)	0.5068 (16)	0.6170 (4)
C(16)	0.4820 (2)	0.9236 (3)	0.1499 (2)	C(16)	0.9105 (7)	0.5810 (13)	0.6671 (4)
C(17)	0.6307 (2)	0.6222 (2)	-0.0002 (1)	C(17)	0.5307 (7)	0.5448 (13)	0.7720 (3)
C(18)	0.6297 (2)	0.5143 (3)	0.0498 (2)	C(18)	0.5710 (8)	0.3584 (14)	0.8021 (4)
C(19)	0.6321 (3)	0.3922 (3)	0.0155 (2)	C(19)	0.4748 (10)	0.2243 (18)	0.8209 (4)
C(20)	0.6382 (3)	0.3790 (3)	-0.0673 (2)	C(20)	0.3361 (10)	0.2752 (20)	0.8082 (5)
C(21)	0.6386 (3)	0.4859 (4)	-0.1166 (2)	C(21)	0.2969 (10)	0.4642 (20)	0.7762 (5)
C(22)	0.6334 (2)	0.6074 (3)	-0.0836 (1)	C(22)	0.3924 (8)	0.5998 (17)	0.7568 (4)
C(23)	0.7980 (2)	0.9674 (3)	0.0299 (2)	C(23)	0.4385 (6)	0.8755 (11)	0.5888 (3)
C(24)	0.8296 (2)	0.8799 (3)	-0.0277 (2)	C(24)	0.4121 (7)	1.0844 (12)	0.6149 (4)
C(25)	0.8890 (3)	0.9195 (4)	-0.0922 (2)	C(25)	0.3288 (8)	1.2104 (14)	0.5692 (4)
C(26)	0.9177 (3)	1.0476 (4)	-0.0979 (3)	C(26)	0.2721 (8)	1.1279 (16)	0.4973 (4)
C(27)	0.8860 (3)	1.1351 (5)	-0.0416 (3)	C(27)	0.2981 (8)	0.9198 (15)	0.4716 (4)
C(28)	0.8268 (3)	1.0963 (3)	0.0219 (2)	C(28)	0.3822 (7)	0.7921 (13)	0.5165 (4)
N(1)	0.8545 (3)	0.7354 (2)	0.1515 (1)	N(1)	0.9642 (6)	0.6703 (10)	0.8484 (3)
N(2)	0.7795 (1)	0.6966 (2)	0.1126 (1)	N(2)	0.8380 (6)	0.6061 (11)	0.8303 (3)
O(1)	0.6767 (1)	0.7289 (2)	0.2453 (1)	O(1)	0.8369 (7)	1.0711 (10)	0.7639 (4)
O(2)	0.5841 (1)	0.8427 (2)	-0.0038 (1)	O(2)	0.5647 (5)	0.8257 (8)	0.7033 (2)
O(3)	0.7141 (1)	1.0084 (2)	0.1533 (1)	O(3)	0.5680 (5)	0.5692 (9)	0.6136 (2)
				Br	1.3607 (1)	0.1571 (2)	1.0444 (0)
Hydrogen Atoms in 1a							
H(1)	1.160 (4)	0.409 (4)	0.183 (3)	H(18)	0.624 (2)	0.523 (3)	0.109 (2)
H(2)	1.152 (3)	0.598 (4)	0.259 (2)	H(19)	0.633 (3)	0.320 (3)	0.051 (2)
H(3)	1.013 (2)	0.741 (3)	0.243 (2)	H(20)	0.644 (3)	0.290 (4)	-0.091 (2)
H(5)	0.875 (3)	0.509 (5)	0.070 (3)	H(21)	0.642 (2)	0.477 (3)	-0.177 (2)
H(6)	1.015 (4)	0.368 (5)	0.081 (3)	H(22)	0.637 (3)	0.684 (3)	-0.118 (2)
H(12)	0.495 (2)	0.694 (3)	0.282 (2)	H(24)	0.806 (3)	0.792 (4)	-0.025 (2)
H(13)	0.327 (3)	0.754 (4)	0.304 (2)	H(25)	0.908 (3)	0.860 (4)	-0.130 (2)
H(14)	0.248 (3)	0.923 (3)	0.228 (2)	H(26)	0.965 (3)	1.072 (4)	-0.143 (3)
H(15)	0.347 (3)	1.029 (4)	0.130 (2)	H(27)	0.903 (3)	1.223 (4)	-0.041 (2)
H(16)	0.521 (2)	0.966 (3)	0.112 (2)	H(28)	0.803 (3)	1.152 (3)	0.062 (2)

^a Estimated standard deviations given in parentheses. ^b Hydrogen atoms in **1a** are given the number of the carbon atom to which they are attached.

Cell Data for α -Phenylazo- β -benzoyloxybenzalacetophenone (2a**).** Bright red prisms of **2a** were obtained from acetone, mp 162°. ¹⁴

Synthesis and Thermal Rearrangement of α -Phenylazo- β -benzoyloxybenzalacetophenone (2a**).** This compound was best prepared by a method based on a study of related compounds by Russell and Weisleder.^{15a} When 5.0 g of diphenyltriketone *sym*-phenylhydrazine in 50 ml of dry pyridine was allowed to react with 7.5 ml of benzoyl chloride at room temperature, the solution became orange and then bright red. After 50 min of stirring, the mixture was added to 300 ml of ether and extracted with ten 150-ml portions of water to remove the pyridine. Approximately 0.3 g of **3a** crystallized at this point and was removed by filtration. The ether solution, when dried with MgSO₄, filtered, and concentrated at room temperature, produced a red oil which gave crystals of **2a**

(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(14) Reflection data out to $2\theta = 110^\circ$ were collected on a crystal of **2a** on the Picker FACS-1 diffractometer (Cu K α radiation) by the general techniques described in this paper. Out of 6166 measurements, 3723 reflections were judged to be significantly above zero at the 2σ level. Considerable effort has thus far failed to provide a solution to this structural problem.

(15) (a) C. S. Russell and D. Weisleder, *J. Org. Chem.*, **32**, 2626 (1967); (b) C. S. Russell, K. Strothkamp, and D. Kasprisin, *ibid.*, **34**, 231 (1969).

when treated with a small amount of absolute ethanol. The product was recrystallized from acetone and purified further by chromatography on Florisil. There was obtained 3 g of **2a**, mp 162°, with an ir spectrum identical with that obtained⁴ previously.

When the solid **2a** was heated in a rotating flask in a constant temperature bath, $140 \pm 0.5^\circ$, there appeared in addition to the expected **3a** about 2% of a new white compound, mp 119–120°, as sublimate which collected in the neck of the flask above the surface of the bath. This compound had the formula C₂₁H₁₆N₂O₂; the similarity of the uv spectrum (CH₂Cl₂), λ_{max} 251 nm (log ϵ 3.97), 287 s (3.72), and 390 (3.93), to that of phenylglyoxal phenylhydrazine in methanol¹⁶ suggests that the compound may be phenylglyoxal benzoylphenylhydrazine. At temperatures below 103° the compound was formed to the extent of less than 1% in the rearrangement of **1a**.

Quantitative Study of the Rearrangement of Phenylazotribenzoylmethane (1a**) to Enol Benzoate (**2a**) and Benzoylhydrazine (**3a**).** Crystals employed for the solid state reaction were grown in tubes purged with argon from solvents which had been triply distilled from LiAlH₄. Results obtained in flasks evacuated during reaction were the same as those carried out under atmospheric pressure. Macroscopic amounts of **1a** were caused to rearrange by heating in

(16) C. F. H. Allen and J. A. vanAllan, *J. Amer. Chem. Soc.*, **73**, 5850 (1951).

a mechanically rotated long-necked flask submersed in a bath maintained within $\pm 0.05^\circ$. Mixtures were analyzed from the spectra (CH_2Cl_2) in the range 410–475 nm, by digitizing at 14 points 5 nm apart. The data, together with those obtained from standard spectra of the pure components, were submitted to a least-squares curve-fitting routine.¹⁷ Use of the method to analyze known mixtures gave results accurate to better than 1%. These data were fitted to a first-order rate expression by a method of least squares,¹⁸ which optimized the infinity point. Points which fell more than two standard deviations from the least-squares line were omitted from the calculation of the rate constant. The plot in Figure 1 shows an induction period followed by a reaction which fits first-order kinetics from 4 to greater than 70% reaction. In Table III are summarized kinetic results. The rate constants

Table III. Rates of Rearrangement of Solid Phenylazotribenzoylmethane (**1a**)

Type of sample	Temp, °C	$k_1 \times 10^6, \text{sec}^{-1}$
Xylene-hexane form		
Crushed	65.0	0.497 ± 0.008
Crystals ^a	75.0	1.31 ± 0.04
Crystals	90.0	25.0 ± 2.0
Crushed	90.0	14.6 ± 0.8
Etherates ^{b,c}		
Pointed	75.0	4.0 ± 0.5
Blunt	75.0	1.5 ± 0.2
Crushed	75.0	0.67 ± 0.04
Pointed	90.0	324 maximum ^d
Blunt	90.0	50 maximum ^d
Crushed	90.0	12.8 ± 0.5
Crude crushed ^e	89.5	22.2 ± 0.5
Pointed	102.8	759 maximum ^d

^a Small clumps of crystals from reagent grade solvents. ^b Had lost ether by evaporation before reaction. ^c Reference 7 describes the preparation and some properties of these crystals. ^d Maximum rate between two points. ^e Partially crushed sample from reagent grade solvent.

reported were obtained from the linear part of the plot after the induction period. In those few cases where there was not a substantial linear portion, the maximum rate estimated from pairs of points was listed.

Chemically Induced Dynamic Nuclear Polarization and Electron Spin Resonance Studies. Proton magnetic resonance spectra of samples of **1a** in hexamethylphosphoramide which had been dried over molecular sieves were observed at 80 ± 2 – $105 \pm 2^\circ$ to give an inverted peak at τ 2.727, with a duration of 485 sec (80°), 755 (90), and 90 (105). The peak corresponded to the position of a resonance observed in the spectrum of the reaction product **3a**. Introduction of benzene showed that the peak was not at the position of the benzene proton resonance.

Solid samples of **1c** which had lost its ether were heated for 40–60 min at 100° and quickly introduced into the cavity of a Varian V-4502 esr spectrometer. A resonance was observed at 3522 G (9.5 GHz) but no fine structure was present. Samples composed of large particles of **1c** appeared to give stronger resonances than finely divided material. Saturated solutions of **1a** in benzene or xylene examined at room temperature or near the boiling points of the solvents showed no esr signal. (The space available in the cavity limited the size of the sample tube to 1 in. of 3-mm quartz tubing).

Results and Discussion

Molecular Dimensions of Phenylazotribenzoylmethane (1a). The bond lengths and angles for **1a** (Table IV) agree with generally accepted values for such dimensions; the C–C lengths in the phenyl rings range from 1.367 (7) to 1.395 (6) Å, while the C–C–C (phenyl) bond angles lie between 118.3 (3) and 121.1 (5) $^\circ$.¹⁰ The N(1)–N(2) bond is clearly a trans double bond with a length of 1.233 (4) Å. The angles at both N(1) and

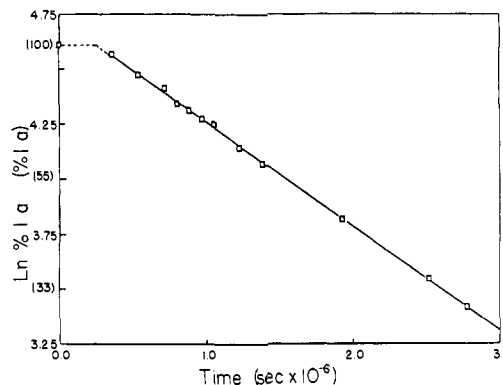


Figure 1. Rearrangement at 65° of **1a** recrystallized from xylene-hexane and crushed. The rate constant from this plot is $4.97 \times 10^{-7} \text{sec}^{-1}$.

Table IV. Bond Lengths (Å) and Angles (deg) in **1a**^a and **2b**^b

1a		2b	
C(7)–C(8)	1.580 (4)	Br–C(1)	1.900 (9)
C(7)–C(9)	1.545 (4)	C(4)–N(1)	1.448 (10)
C(7)–C(10)	1.557 (4)	N(1)–N(2)	1.279 (8)
C(8)–C(11)	1.487 (4)	N(2)–C(7)	1.401 (10)
C(9)–C(17)	1.490 (4)	C(7)–C(8)	1.497 (11)
C(10)–C(23)	1.491 (5)	C(8)–O(1)	1.206 (10)
N(1)–C(4)	1.443 (5)	C(8)–C(11)	1.494 (11)
N(1)–N(2)	1.233 (4)	C(7)–C(9)	1.381 (11)
N(2)–C(7)	1.479 (4)	C(9)–O(2)	1.420 (9)
C(8)–O(1)	1.215 (4)	C(9)–C(17)	1.433 (11)
C(9)–O(2)	1.210 (4)	C(10)–O(2)	1.369 (8)
C(10)–O(3)	1.210 (4)	C(10)–O(3)	1.195 (9)
		C(10)–C(23)	1.453 (10)
C(8)–C(7)–N(2)	106.6 (2)	Br–C(1)–C(2)	118.5 (5)
C(9)–C(7)–N(2)	107.9 (2)	Br–C(1)–C(6)	116.1 (7)
C(10)–C(7)–N(2)	111.8 (2)	C(3)–C(4)–N(1)	112.7 (4)
C(8)–C(7)–C(9)	113.2 (2)	C(5)–C(4)–N(1)	124.4 (5)
C(8)–C(7)–C(10)	107.6 (2)	C(4)–N(1)–N(2)	112.2 (4)
C(9)–C(7)–C(10)	109.7 (3)	N(1)–N(2)–C(7)	109.3 (6)
C(7)–N(2)–N(1)	114.1 (2)	N(2)–C(7)–C(8)	119.4 (4)
C(4)–N(1)–N(2)	112.2 (2)	N(2)–C(7)–C(9)	118.1 (5)
C(3)–C(4)–N(1)	115.9 (3)	C(8)–C(7)–C(9)	122.3 (7)
C(5)–C(4)–N(1)	123.2 (3)	C(7)–C(8)–O(1)	120.7 (6)
C(7)–C(8)–C(11)	122.2 (3)	C(7)–C(8)–C(11)	118.0 (5)
C(7)–C(8)–O(1)	117.1 (3)	O(1)–C(8)–C(11)	121.1 (7)
C(11)–C(8)–O(1)	120.7 (2)	C(8)–C(11)–C(12)	117.6 (7)
C(8)–C(11)–C(12)	116.1 (3)	C(8)–C(11)–C(16)	120.9 (6)
C(8)–C(11)–C(16)	124.5 (2)	C(7)–C(9)–O(2)	112.0 (4)
C(7)–C(9)–C(17)	119.1 (2)	C(7)–C(9)–C(17)	132.8 (5)
C(7)–C(9)–O(2)	119.0 (2)	O(2)–C(9)–C(17)	115.0 (7)
C(17)–C(9)–O(2)	121.7 (3)	C(9)–C(17)–C(18)	122.7 (7)
C(9)–C(17)–C(18)	122.9 (3)	C(9)–C(17)–C(22)	116.4 (7)
C(9)–C(17)–C(22)	116.8 (3)	C(9)–O(2)–C(10)	116.7 (6)
C(7)–C(10)–C(23)	118.3 (2)	O(2)–C(10)–O(3)	121.4 (6)
C(7)–C(10)–O(3)	119.4 (2)	O(2)–C(10)–C(23)	111.7 (5)
C(23)–C(10)–O(3)	122.3 (3)	O(3)–C(10)–C(23)	126.7 (5)
C(10)–C(23)–C(24)	123.8 (3)	C(10)–C(23)–C(24)	122.1 (7)
C(10)–C(23)–C(28)	117.7 (3)	C(10)–C(23)–C(28)	116.9 (6)

^a The C–C(phenyl) lengths range from 1.367 (7) to 1.395 (6) Å. The complete list has been deposited (ref 10). The C–H lengths range from 0.92 to 1.06 Å (esd 0.03–0.05 Å). The C–C–C(phenyl) angles range from 118.3 (3) to 121.1 (5) $^\circ$. The C–C–H angles range from 114 to 125 $^\circ$ (esd 2–3 $^\circ$). ^b The C–C(phenyl) lengths range from 1.334 (14) to 1.464 (16) Å and the C–C–C(phenyl) angles range from 115.8 (9) to 125.3 (5) $^\circ$; the complete list has been deposited.¹⁰

N(2) are much less than 120 $^\circ$, however, being 112.2 (2) and 114.1 (2) $^\circ$, respectively.

Molecular Conformation. A comparison of the molecular structure of **1a** with the corresponding

(17) A detailed description and listing of this program are presented in the Ph.D. Thesis of D. B. P., Jr.

(18) J. P. Petrovich, Ph.D. Thesis, University of Illinois, 1964.

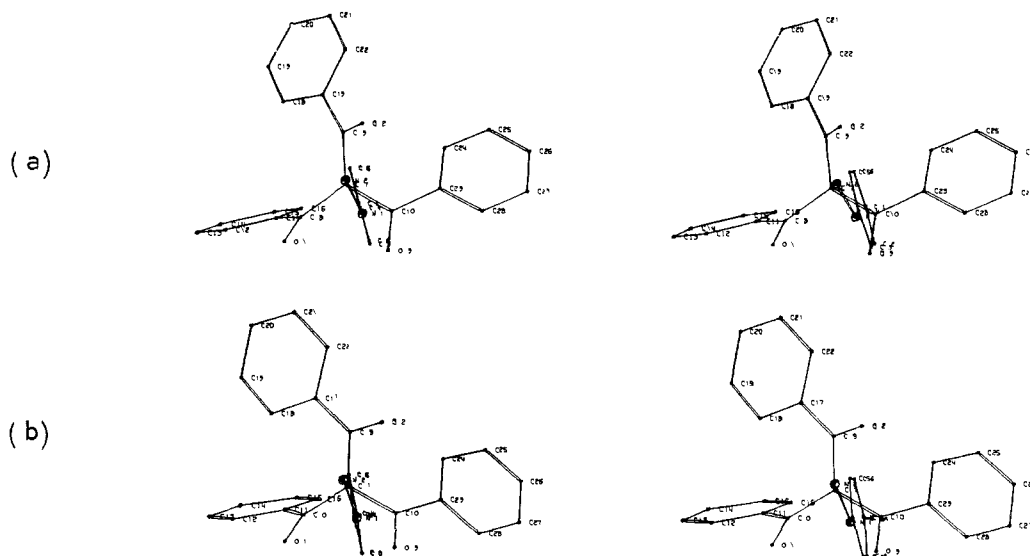


Figure 2. (a) Stereoscopic drawing of a single molecule of **1a** viewed along the C(7)–N(2) bond. (b) Stereoscopic drawing of a single molecule of **1b** viewed along the same bond and in the same orientation.

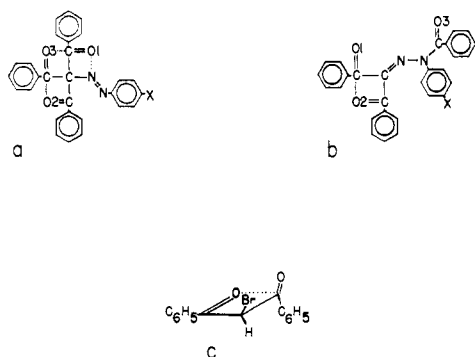


Figure 3. (a) Schematic drawings showing the C...O interaction in **1**, (b) in **3**, and (c) in the keto form of dibenzoylbromomethane.

bromo derivative **1b**⁸ shows remarkable similarity in the conformations of the two molecules (Figure 2). The greatest difference in torsion angles¹⁰ in the central portions of the two molecules is 24°. The introduction of the bromine atom has thus altered substantially the crystal packing but not the molecular conformation. It is evident that in each structure the conformation is that in which one carbonyl oxygen atom is pointed approximately toward an azo nitrogen atom with a second carbonyl oxygen toward the carbonyl carbon of the first and a third carbonyl oxygen toward the carbon of the second carbonyl group, a situation which can be represented schematically as shown in Figure 3a. The distances between all the pairs of atoms discussed fall between 2.61 and 2.76 Å.¹⁰ It seems likely that these nonbonded interactions have a part in determining the molecular conformation in the crystal. Examination of the structure of diphenyl triketone benzoylphenylhydrazine (**3a**)¹⁹ shows that here also the molecular conformation is such as to permit an oxygen–carbon interaction (2.68 (1) Å) of the same type (Figure 3b). A recent electron-diffraction determination²⁰ of the

(19) D. B. Pendergrass, Jr., I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **94**, 8730 (1972).

(20) A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *ibid.*, **93**, 6399 (1971). Coordinates of C(4) and C(5) are interchanged in Table II of this paper.

structure of acetylacetone in the vapor state at 105° gave values of atomic coordinates from which the calculated O...C distance in the keto tautomer is 2.86 Å. X-Ray crystal structures have shown *cis*-1,2-dibenzoyl-ethylene and its *p,p'*-dichloro derivative to exist in conformations that permit similar interactions with oxygen–carbon distances of 2.67 (1) and 2.85 (1) Å. Here introduction of the chlorine atom has required a substantial alteration in crystal packing but not in molecular configuration.²¹

While the intramolecular carbonyl–carbonyl interaction appears to be a significant factor in fixing the conformation of molecules with 1,3-diketone groups, it may not be a sufficiently strong intermolecular interaction to govern the packing of ketones. For example, there is no such short carbonyl–carbonyl distance in the crystal structures of benzophenone, α -chloroacetophenone, several 4-acetylbiphenyls, benzil, pyridil, or anthrone.²² There are a few examples^{23,24} of such short intermolecular interactions, however.

It seems likely that these intramolecular interactions may play a significant part in determining conformational equilibria of compounds in solution as well as in the solid state. For example, the conformation of *cis*-dibenzoyl-ethylene in the crystalline state is similar to the conformation of *cis*-phenyldibenzoyl-ethylene in solution as deduced²⁵ from spectral evidence. Furthermore, an interaction of the sort discussed here may provide a partial explanation for the observation that in the case of the phenyldibenzoyl-ethylenes the *cis* isomer is more stable than the *trans*. The possible significance of the conformation found in the crystalline state of *cis*-dibenzoyl-ethylene to a photochemical rearrangement

(21) D. Rabinovich, G. M. J. Schmidt, and Z. Shaked, *J. Chem. Soc. B*, 17 (1970).

(22) See O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Vol. I, International Union of Crystallography, 1970, for references.

(23) C. A. Maier, J. A. Kapecki, and I. C. Paul, *J. Org. Chem.*, **36**, 1299 (1971); B. Krebs and D. F. Koenig, *Acta Crystallogr., Sect. B*, **25**, 1022 (1969).

(24) Literature cited in ref 21 and 23.

(25) L. P. Kuhn, R. E. Lutz, and C. R. Bauer, *J. Amer. Chem. Soc.*, **72**, 5058 (1950).

found in solution has already been noted.²¹ Finally the curious infrared spectrum of the keto form of dibenzoylbromomethane (two strong partially resolved peaks centered at 1708 and 1682 cm^{-1}) which had been observed²⁶ in chloroform solution could be explained by a locking of the molecule in a conformation such as that shown in Figure 3c with the carbonyl group oriented cis to the bromine atom. The effect of an α -bromine substituent on the frequency of carbonyl absorption is well known²⁷ to result in an angularly dependent frequency shift which amounts to about 20 cm^{-1} when the carbonyl group and bromine are nearly cis and coplanar. In the conformation shown, the orientation of the bromine is such that it might be expected to shift to higher frequency the stretching vibration of one carbonyl group and not the other.

Many of the features of the molecular conformations discussed in the present section may also be influenced by the tendency of the carbonyl group to be eclipsed with an α, β C-C bond. This tendency has been rationalized by treating the C=O double bond as two bent single bonds,^{28, 29} so that the conformation where the α, β C-C bond eclipses the C=O double bond is considered really to be one with the C-C bond bisecting the two bent single bonds.

Crystal Packing. In view of the tendency for both **1a** and **1b** to undergo solid state rearrangements, the differences in the packing of the two compounds deserve examination. Intermolecular contacts < 3.7 Å for **1a** and **1b** are listed in Table V. Packing diagrams of **1a** and **1b**, oriented to look along the C(7)-N(2) bond in the basic molecules in each case, are shown in Figure 4. In **1a**, phenyl ring B is positioned at right angles between ring C^{II} (see Table V) and ring C^{VII}. Ring B is also quite close to O(1)^{VI}. Phenyl ring C is close and parallel to the same ring in molecule II and is involved in the previously described contacts with ring B in other molecules. C(22) is close to O(1)^I. Ring D is quite close and parallel to ring D^V and is nearly normal to ring A^I and ring A^V. In **1b**, ring B is positioned nearly at right angles between rings C^{VIII} (see Table V) and D^{IX}. Rings C and D sit in pockets created by several surrounding phenyl rings. Apart from a rather similar environment for ring B, the packing in the two crystals is quite different. The major difference in the molecules, the bromine atom in **1b**, is thrust into the cavity created by O(1), O(3), and N(1) in molecule VII; there are Br---O(1)^{VII} and Br---N(1)^{VII} distances of 3.22 and 3.44 Å. There do not appear to be any very close contacts in the corresponding cavity in the crystal of **1a**.

The shortest distance between potential reacting centers in **1a** is 4.79 Å between C(9) and O(1)^I (Table V) and in **1b** is 4.99 Å between C(9) and O(3)^I.

Molecular Dimensions of α -*p*-Bromophenylazo- β -benzoyloxybenzalacetophenone (2b**).** Some bond lengths and angles for **2b** are given in Table IV. The mean value for the 24 C-C(aromatic) bond lengths is 1.40 Å with a rms deviation of 0.02 Å.¹⁰

(26) M. L. Poutsma, Ph.D. Thesis, University of Illinois, Urbana, 1962.

(27) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1958, pp 139 ff.

(28) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 136-138.

(29) J. D. Dunitz and P. Strickler, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 595-602.

Table V

Intermolecular Contacts < 3.7 Å for 1a			
C(22)---O(1) ^I	3.35	C(19)---C(22) ^{II}	3.66
C(11)---C(20) ^{II}	3.65	C(15)---O(2) ^{III}	3.37
C(12)---C(20) ^{II}	3.64	C(16)---O(2) ^{III}	3.52
C(12)---C(21) ^{II}	3.66	C(1)---C(21) ^{IV}	3.64
C(17)---C(19) ^{II}	3.44	C(3)---C(26) ^V	3.62
C(18)---C(20) ^{II}	3.68	C(14)---O(1) ^{VI}	3.47
C(18)---C(21) ^{II}	3.69	C(15)---O(1) ^{VI}	3.26
I, $x, 1/2 - y, -1/2 + z$		C(13)---O(3) ^{VIII}	3.45
II, $1 - x, 1 - y, -z$		C(2)---O(3) ^{IX}	3.33
III, $1 - x, 2 - y, -z$		V, $2 - x, 2 - y, -z$	
IV, $2 - x, 1 - y, -z$		VI, $1 - x, 1/2 + y, 1/2 - z$	
		VII, $x, 1/2 - y, 1/2 + z$	
		VIII, $1 - x, -1/2 y, +1/2 - z$	
		IX, $2 - x, -1/2 + y, 1/2 - z$	
Intermolecular Contacts < 3.7 Å for 1b			
C(2)---C(22) ^I	3.69	C(25)---C(26) ^V	3.63
C(2)---O(2) ^I	3.36	C(26)---C(26) ^V	3.62
C(3)---O(2) ^I	3.69	C(5)---O(3) ^{VI}	3.42
C(27)---O(1) ^{II}	3.42	C(20)---C(27) ^{VI}	3.63
C(3)---C(13) ^{III}	3.63	Br---N(1) ^{VII}	3.44
C(19)---O(1) ^{IV}	3.35	Br---O(1) ^{VII}	3.22
I, $1 + x, y, z$		V, $-x, 1 - y, 1 - z$	
II, $x, 1/2 - y, 1/2 + z$		VI, $-x, 1/2 + y, 1/2 - z$	
III, $1 + x, 1/2 - y, 1/2 + z$		VII, $1 - x, 1/2 + y, 1/2 - z$	
IV, $-x, 1 - y, -z$		VIII, $-1 - x, 1 - y, -z$	
		IX, $-x, -1/2 + y, 1/2 - z$	
Intermolecular Contacts < 6 Å between Potential Reacting Centers			
1a		1b	
C(9)---O(1) ^I	4.79	C(9)---O(3) ^I	4.99
C(8)---O(2) ^{II}	5.30	C(10)---O(3) ^I	5.92 ^a
C(8)---O(2) ^{III}	5.70	C(10)---N(1) ^{II}	5.92
C(9)---O(2) ^{III}	5.01 ^a		
C(9)---O(3) ^{III}	5.92		
C(10)---O(2) ^{III}	5.01		
C(8)---O(3) ^{IV}	5.96		
I, $x, 1/2 - y, -1/2 + z$		I, $-x, 1/2 + y, 1/2 - z$	
II, $x, 1/2 - y, 1/2 + z$		II, $-x, -1/2 + y, 1/2 - z$	
III, $1 - x, 2 - y, -z$			
IV, $1 - x, -1/2 + y, 1/2 - z$			

^a These contacts would require one benzoyl group to migrate to the corresponding group in the next molecule and would thus require a very complex mechanism.

The stereochemistry about the N=N double bond is trans (Figure 5), while the carbonyl group [C(10)-O(3)], which migrates in the isomerization of **2b** to **3b**, and the receiving *p*-bromophenylazo group are trans with respect to the C=C double bond. The central N(2)-C(7)=C(9)-C(17) group is accurately planar while the attached atoms O(2) and C(8) deviate by 0.07 and 0.04 Å, respectively, in opposite directions from the mean plane. The N=N bond length of 1.279 (8) Å is longer than that (1.233 (4) Å) in **1a**. The N(2)-C(7) length (1.401(10) Å), as compared to 1.479 (4) Å for the C(7)-N(2) bond in **1a**, implies considerable conjugation between the N(1)-N(2) and C(7)-C(9) double bonds, a conclusion that would be consistent with the lengths found for these double bonds. Both carbonyl groups in **2b** lie on the same side of the double bond (cis) but point in opposite directions.

Crystal Packing. The molecules of **2b** pack in long stacks along the *b* axis (6.309 Å) with the oxygen atom of the C(8)=O(1) carbonyl group thrust into a cavity formed by C(5), N(2), and C(18) of the adjacent molecule; the distances from O(1) to those three atoms are 3.26, 3.46, and 3.41 Å, respectively. Other packing forces acting on the molecule may result from the C(19)···O(2) interaction (3.46 Å) with the molecules

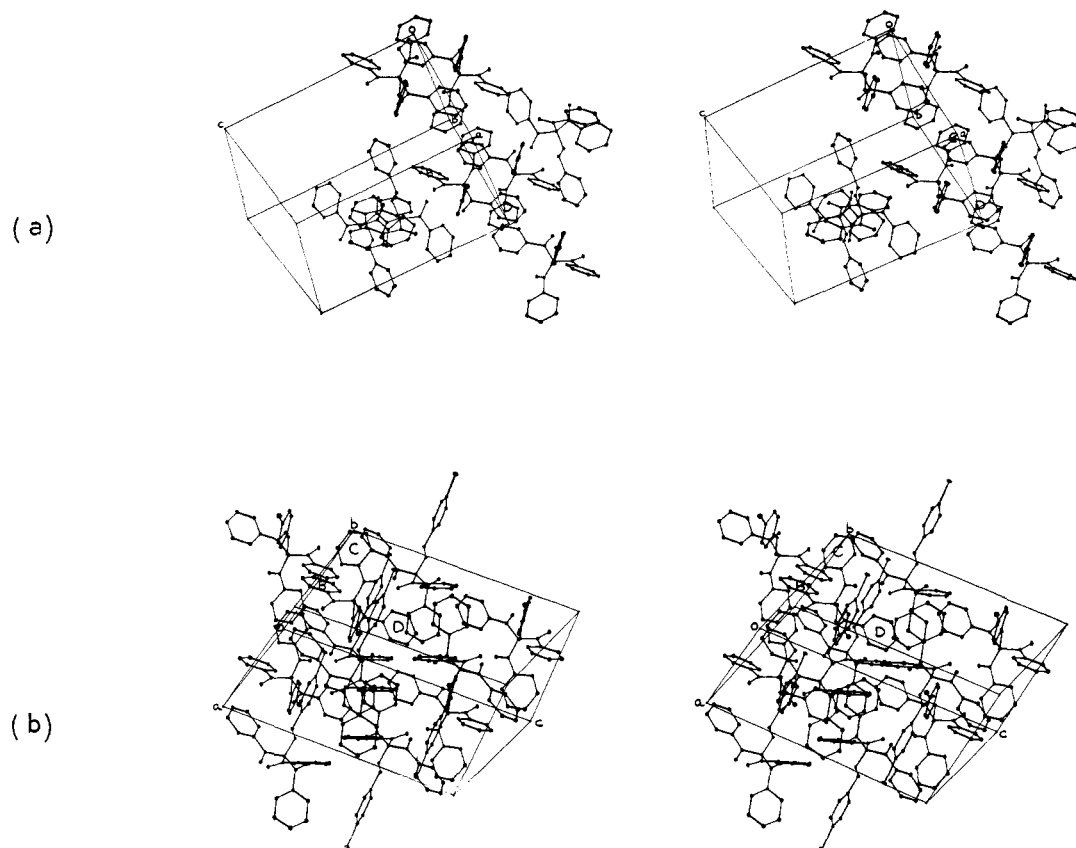


Figure 4. Stereoscopic views of the crystal packing of (a) **1a** and (b) **1b** with the unit cells oriented so that one is looking along the C(7)-N(2) bond in the basic molecule in each case. In the basic molecule the rings in the three benzoyl groups are marked B, C, and D.

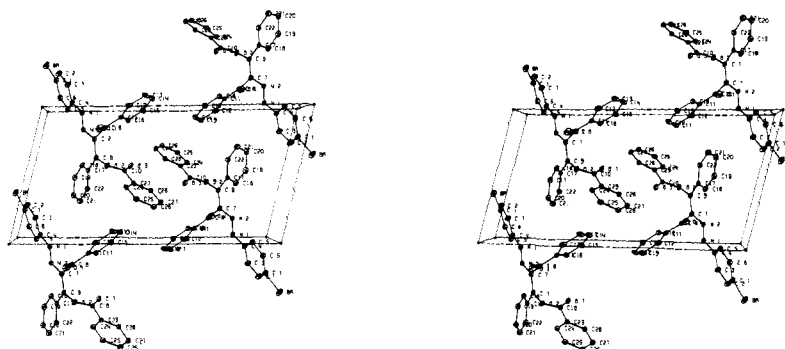


Figure 5. Stereoscopic view of the packing in the crystal of **2b**.

related by a unit translation along b and the C(21)···C(3) interaction (3.51 Å) between atoms related by unit translations along the a axis. The orientation of the C(10)-C(23)-O(3) benzoyl group places the carbonyl oxygen atom 3.32 Å from C(28) in a molecule related by an inversion center (Figure 5). Other close contacts with the benzoyl group include O(3)···C(25) and O(3)···C(24) distances of 3.17 and 3.42 Å, respectively, between stacks of molecules parallel to the b axis. The shortest intermolecular contact between N(1) and C(10) of the migrating benzoyl group is 7.48 Å compared with the intramolecular distance of 5.33 Å.

Solid State Rearrangement of Phenylazo Triketone 1a. The azo triketone **1a** or its bromo derivative **1b** when mixed with the products of their rearrangements **2** and **3** had a eutectic temperature of approximately 115–

120°. An earlier examination⁶ of the solid state rearrangement of **1b** suffered from the dual disadvantages that the temperature employed (105°) was closer to the eutectic temperature than was desirable and that the use of a Kofler hot stage could possibly result in uneven heating.³⁰ For this reason quantitative studies of the rearrangement of **1a** were carried out in a rotating long-necked flask immersed in a constant temperature bath. Analyses of portions of a sample heated under these conditions and withdrawn after varying periods of time were carried out with crystals of **1a** as obtained by crystallization from xylene-hexane and after crushing. Studies were also made on the etherate **1c'** which had been allowed to lose its incorporated ether. Tempera-

(30) Insertion of a thermister as a temperature probe immediately above the surface of the hot stage indicated that even with the cover in place there is a temperature gradient of over 5°/mm.

tures employed ranged from 65 to 103°. Crystals from xylene-hexane at 65° showed an induction period after which time the data for the reaction from 4 to more than 70% completion fitted a first-order rate law satisfactorily (see Figure 1 in the Experimental Section). Observation of individual crystals with a polarizing microscope, however, showed that the same erratic behavior which had been observed previously in the rearrangement of **1b** on the hot stage had occurred; parts of a crystal had rearranged extensively when at the same time other regions of the same crystal or adjacent crystals remained with no visible change. It can only be concluded that the first-order behavior observed is average behavior of various crystal regions whose individual behavior must differ greatly from the average; such a rate measurement cannot have the same kind of mechanistic significance it has in solution chemistry. Such first-order behavior is rare in solid state chemistry but has been observed in the thermal racemization of (+)-bicyclo[2.2.1]hept-5-ene-*trans*-2,3-dicarboxylic acid^{31a} and in the rearrangements of benzophenone oxime *O*-picryl ethers.^{31b} The more common behavior has been that observed in the rearrangement of *cis*- to *trans*-azobenzene which followed the Prout-Tomkins equation.^{31c} In spite of the difficulties associated with mechanistic interpretation of the data, it may be noted that comparison of first-order rate constants calculated from that part of the reaction which occurs after the induction period leads to several conclusions which seem to hold throughout the work. The crystals of **1a** from xylene-hexane rearranged at approximately the same rate as the etherate which had lost its ether; in each case crushed crystals rearranged at a rate which was slower by a factor of 2 or more (see Table III).³² At the same time the induction periods appeared to be shortened by crushing. The ratio of the solid-state reaction to the rate previously observed⁴ in benzene solution is of the order of 1/10², a value consistent with that previously observed for the bromo compound **1b**.⁶

The effect of the solid state on the ratio of **2a** to **3a** produced was striking in several respects. Data accumulated from the reactions of **1a**, or **1c** which had lost its ether, and with samples crushed or uncrushed, showed that the ratio of products was independent of the treatment of starting crystals before reaction and of the extent of reaction but was significantly dependent on the temperature. Results are shown in Figure 6. It can be seen that the product ratio **2a/3a** varies from 0.5 at 65° to 1.21 at 102.8°. This may be compared with the ratios⁴ in dioxane solution which ranged from 0.97 at 58.8° to 0.92 at 77.1°, the effect of a temperature increase raising the ratio in the solid state. As was found for the bromo derivative **1b**, examination of the molecular structure of **1a** (Figure 2) suggests that there should be no strong bias in favor of migration of a benzoyl group either to an adjacent carbonyl oxygen (formation of the enol benzoate **2a**) or to doubly bound

(31) (a) R. E. Pincock, M.-M. Tong, and K. R. Wilson, *J. Amer. Chem. Soc.*, **93**, 1669 (1971); (b) J. D. McCullough, Jr., D. Y. Curtin, and I. C. Paul, *ibid.*, **94**, 874 (1972); (c) M. Tsuda and K. Kuratani, *Bull. Chem. Soc. Jap.*, **37**, 1284 (1964).

(32) As indicated in Table III the "blunt" crystals of **1c** after loss of ether appeared to react more slowly than the "pointed" crystals by a factor of 2. Since X-ray examination has indicated that the two types of crystals have the same internal structure this point requires further investigation.

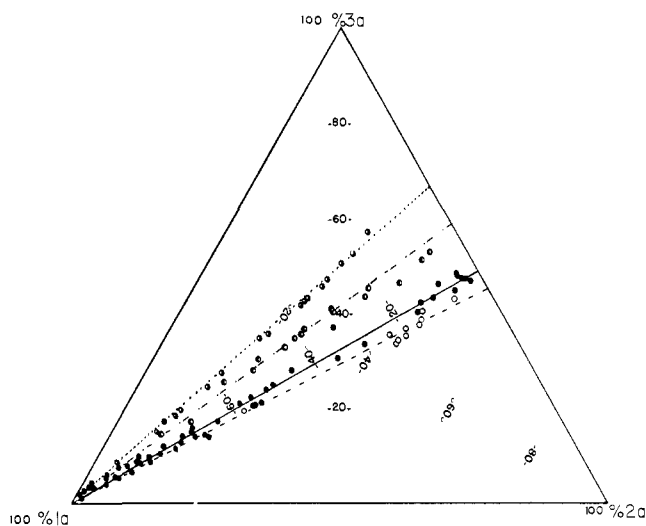


Figure 6. Ratio of products determined from a plot of the compositions of reaction mixtures from the rearrangement of **1a**. Ratios **2a/3a** were obtained by extrapolation of the weighted least-squares lines through each set of points to 0% **1a**. The dotted line and circles with their right halves blackened are data at 65.0° and give an extrapolated ratio of 0.494. The dotted and dashed line and circles with their left halves blackened are data at 75.0° and gave an extrapolated ratio of 0.694. The completely filled circles and solid line are data at 90.0° and gave an extrapolated ratio of 1.04. Unfilled circles and the dashed line are from data at 102.8° and gave an extrapolated ratio of 1.21.

nitrogen atom (formation of benzoylhydrazone **3a**). The intramolecular carbonyl interactions hold the molecule of **1a** in a position (Figures 2 and 3) such that C(10) is quite close to O(2) (where migration would produce **2a**) and to N(1) (where migration would produce **3a**); the C(10)---O(2) and C(10)---N(1) distances are 2.758 (4) and 2.698 (4) Å. Similarly C(8) is 2.667 (4) Å from O(3) (to produce **2a**) and 2.998 (5) Å from N(1) (to produce **3a**). The C(10)C(7)C(9)O(2) and C(10)-C(7)N(2)N(1) torsion angles are -28.6 and 35.8°, respectively, while the C(8)C(7)C(10)O(3) and C(8)C(7)-N(2)N(1) angles are -0.8 and -81.6°. There are no correspondingly short (<3.45 Å) C---O or C---N distances involving C(9). Unfortunately, the benzoyl groups have not been labeled in a way which permits this hypothesis to be examined. In the absence of definite knowledge as to which benzoyl group or groups migrate, it is not possible to rationalize the temperature dependence of the product ratio with the crystal packing. The observations reported in the Experimental Section that an esr signal and chemically induced dynamic nuclear polarization were observed imply that the reaction may not be a simple intramolecular change.

The conclusion from the X-ray structure that the configuration at the carbon-carbon double bond of the enol benzoate is *trans* (Figure 5) in **2b** has substantial mechanistic importance. It was proposed earlier^{4b} that the relatively slow rate of the rearrangement of **2** to **3** might be due to an unfavorable steric orientation of the benzoyloxy carbonyl group with respect to the doubly bound nitrogen atom. In a study of a comparable rearrangement of enol *para*-substituted benzoates **4** to the corresponding benzoylhydrazones **5**, Russell, Strothkamp, and Kasprisin^{15b} have presented elegant evidence that the geometry at the carbon-carbon double

