The Crystal Structure and Solid-State Rearrangement of *p*-Bromobenzeneazotribenzoylmethane[1]

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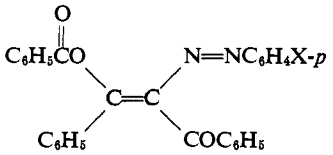
Abstract: A single crystal X-ray structure analysis of the yellow coupling product of the sodium salt of tribenzoylmethane with *p*-bromobenzenediazonium ion has confirmed the C-azo structure previously assigned[4] and established the stereochemistry at the nitrogen–nitrogen double bond as *trans*. The competing reactions with migration of acyl groups from carbon to oxygen and to nitrogen atoms to form the red α-*p*-bromobenzeneazo-β-benzoyloxybenzalacetophenone and white diphenyl triketone *sym*-benzoyl-*p*-bromophenylhydrazone have been studied in the solid phase (105°) and in dioxane solution (59°). Product ratios show only small differences between the solid (0.85) and solution (1.05) reactions. Interatomic distances as determined in the X-ray structure analysis suggest that the crystal lattice provides no strong preference for either rearrangement path as compared to the other. Microscopic examination and chemical analysis shows that rearrangement rates vary from one crystal to the other. Rearrangement often begins in a region of the crystal where there is visible disorder and spreads through the crystal —fastest in a plane normal to the long axis of the crystal. X-Ray examination of the rearranged powder shows no lines clearly to be assigned to the red enol benzoate but sharp lines due to the white benzoylhydrazone, which however is significantly volatile under the reaction conditions. Chemical analysis of single crystals after heating supports quantitatively the qualitative results of microscopic observation and shows that rearrangement is at least 100 to 400 times as fast in solution as it would be in the crystal were the reaction there first order; in more perfect crystals reactivity may be greatly reduced.

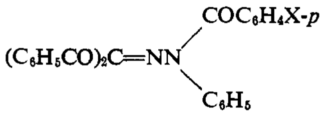
The yellow product formed[3] from the reaction of benzenediazonium fluoroborate with sodium tribenzoylmethide has been inferred,[4] primarily on the basis of the infrared spectrum, to be benzeneazotribenzoylmethane (I) rather than the O-coupled product originally suggested. No direct evidence as to the stereochemistry around the nitrogen–nitrogen double bond has been availabe although it might be expected that the compound should be the *trans* isomer which is much less sterically strained than the *cis*. The yellow benzeneazo compound I undergoes competing rearrangements to the red enol benzoate II and to the white benzoylphenylhydrazone III.[3,4] These rearrangements which are kinetically first order to greater than 90% completion occur at nearly equal rates at 59° in dioxane[4] and at nearly the same rates in the less polar solvent benzene.[5] Attempts to find evidence for radical or ion pair intermediates have been unsuccessful,[4,5] and it is concluded that although such intermediates may be involved they are probably held together by loose bonds with relaxed stereochemical requirements so that the two reactions I → II and I → III may be classed as "intramolecular" isomerizations at least in the sense that the reaction intermediates either do not intervene or are difficult or impossible to trap. A third reaction, the isomerization of the red enol benzoate II to the white hydrazone III, occurs in solution but at a rate less than one-fiftieth the rate of the other two rearrangements.

$(C_6H_5CO)_3CN{=}NC_6H_4X\text{-}p$

I, X = H
IV, X = Br
(yellow)



II, X = H
V, X = Br
(red)



III, X = H
VI, X = Br
(white)

One of the striking characteristics of these rearrangements was that they appeared to occur in the solid state and with the ratio of products II:III significantly higher than in solution.[4] Solid-state reactions of molecular crystals[6] have only recently begun to receive the serious attention of the chemist.[7-10] Although a few isolated

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(2) Allied Chemical and Dye Fellow, 1962–1963; Lubrizol Corporation Fellow, 1963–1964.

(3) O. Dimroth and M. Hartmann, *Ber.*, 40, 2404, 4460 (1907); 41, 4012 (1908).

(4) D. Y. Curtin and M. L. Poutsma, *J. Am. Chem. Soc.*, **84**, 4887, 4892 (1962).

(5) L. L. Miller, Ph.D. Thesis, submitted to the University of Illinois, 1964.

(6) We prefer to classify crystals as "ionic" (*e.g.*, cesium chloride), "covalent" (*e.g.*, diamond), and "molecular" (*e.g.*, most organic solids), defined as "symmetric arrays of weakly interacting molecules," rather than the commonly used but less apt terms "organic" and "inorganic."

(7) M. D. Cohen and G. M. J. Schmidt in "Reactivity of Solids," J. H. de Boer, *et al.*, Ed., Elsevier Publishing Co., Amsterdam, 1961, p 556 ff.

(8) (a) H. Morawetz in "Physics and Chemistry of the Organic Solid State," Vol. I, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 4 (and *Addendum*, Vol. II, p 853 ff); (b) H. S. A. Gilmour, ref 8a, Chapter 5.

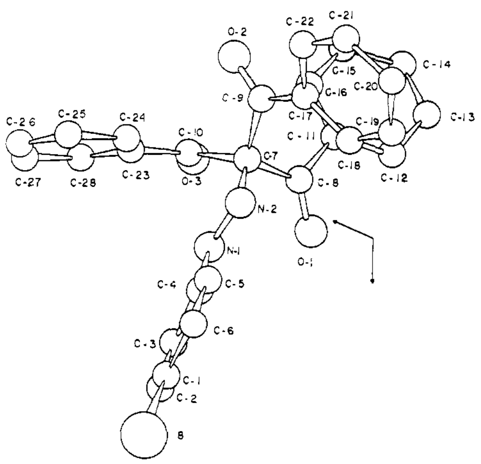

Figure 1. Projection of the structure of the bromo azo triketone IV on the *ac* plane.

examples of isomerization reactions have been supposed to occur in the solid state,[11] almost nothing is known about the details of such reactions which might be expected to show marked differences from solid-state intermolecular or photochemical reactions. The freedom from by-products of the rearrangements of I to II and III and the ease with which the reactions could be followed visually and with chemical methods prompted the further study of this system. The structure I was modified (by the introduction of a bromine atom) to *p*-bromobenzeneazotribenzoylmethane (IV) for convenience in carrying out a single-crystal structure determination.[12] Interest in a complete single-crystal structure of I or IV was prompted by the observation in the photochemical dimerization of *trans*-cinnamic acids[13] that there was a correlation between the structure of the product formed and the initial interatomic distances in the crystal of *trans*-cinnamic acid; carbon atoms which became bonded during the reaction were not more than about 4.1 A apart in the crystal of starting material. In addition, the complete X-ray analysis of IV would settle beyond any doubt the structure and in particular the question of the stereochemistry at the nitrogen–nitrogen double bond.

Determination of the Crystal Structure of *p*-Bromobenzeneazotribenzoylmethane (IV). Crystals of the parent benzeneazo compound I from xylene–hexane and of the *p*-bromo compound[3] IV from benzene–hexane or ether were solvent-free and suitable for X-ray examination. The space group and unit cell dimensions of crystals of these two substances, determined from precession photographs,[14] are presented in Table I, together with the density and number of molecues (N) per unit cell. It had been hoped that the two substances would be isomorphous, which might have permitted the solution of the structure of the bromo compound IV to be used for the solution of the unsubstituted compound I.[15] It can be seen from the crystal data of Table I that the two compounds are not isomorphous. For this reason all further work, both crystallographic and chemical, to be reported here has been carried out with the *p*-bromo compound IV.

Table I. Crystallographic Data for Benzeneazotribenzoylmethane (I) and *p*-Bromobenzeneazotribenzoylmethane (IV)

	Parent compound (I)	Bromo compound (IV)
Space group	$P2_1/c$	$P2_1/c$
Density, g/cc	1.28	1.39
Density calcd for N = 4, g/cc	1.28	1.41
a, A	13.04 ± 0.04	9.84 ± 0.03
b, A	10.34 ± 0.03	14.19 ± 0.04
c, A	16.51 ± 0.05	18.56 ± 0.05
β	90° 45′ ± 10′	111° 50′ ± 10′

The structure of IV was determined by Fourier techniques plus a least-squares refinement with the aid of an IBM 7094 computer. A preliminary attempt to obtain the fractional coordinates of the bromine atoms from a two-dimensional Patterson map computed from precession photographs was unsuccessful. The bromine atoms were located using a three-dimensional Patterson vector map calculated from Weissenberg intensity data (1303 reflections) and the bromine fractional coordinates used to calculate trial structure factors. Several cycles of refinement by Fourier synthesis techniques were followed by a three-dimensional full-matrix least-squares treatment. In Table II are presented coordinates of each atom of one molecule as fractions of the lengths of the unit cell edges as well as the thermal parameters[16a] B and b_{ij}. In Figure 1 is shown a projection of a molecule along the b axis. The final residual R[16b] was 9.87% with all 1303 reflections weighted equally. A further check on the accuracy of the structure is provided by the comparison of bond lengths (Table III) with those to be expected.[17] For example, the average of the 24 carbon–carbon bond lengths and rms deviations in the four benzene rings was 1.41 ± 0.03 A as compared with 1.40 A expected.

The X-ray results fully confirm the gross structural assignment to the C-azo triketone IV and also show the stereochemistry at the nitrogen–nitrogen double bond to be *trans*.

Another point of particular interest in the structure of IV comes from a consideration of distances between the three carbonyl carbon atoms C(8), C(9), and C(10) and the oxygen atoms O(1), O(2), and O(3) to which they could migrate to form the enol benzoate V; these may be compared with the distances from the same three carbon atoms to N(1), the nitrogen atom to which migration must occur if formation of hydrazone VI is to take place. These distances are summarized in Table III.

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[9] H. Morawetz, S. Z. Jakabhazy, J. B. Lando, and J. Shafer, *Proc. Natl. Acad. Sci. U. S.*, **49**, 789 (1963).

[10] H. Morawetz, *Science*, **152**, 705 (1966).

[11] Reference 8a, pp 294–297.

[12] In view of the structural complexity of compounds I, II, and III a limited effort, as yet unsuccessful, was made[5] to find a simpler structural analog of I for study. For example, benzeneazobenzoyldiphenylmethane, structure I with two benzoyl groups replaced by phenyls, failed to undergo benzoyl migration but instead decomposed by cleavage of a carbon–nitrogen bond in what was probably a free radical reaction.

[13] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1996 (1964), and following papers.

[14] M. J. Buerger, "The Precession Method," John Wiley and Sons, Inc., New York, N. Y., 1964.

[15] J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, p 147 ff.

[16] M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960: (a) pp 589–590, 613; (b) p 586.

[17] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958; Supplement, Special Publication No. 18, 1965.

Table II. Final Atomic Positions and Thermal Parameters

Atom	X	Y	Z	B
C(1)	0.5079	0.6154	0.2672	2.82
C(2)	0.5442	0.5211	0.2757	3.76
C(3)	0.4271	0.4548	0.2586	3.82
C(4)	0.2831	0.4897	0.2266	2.75
C(5)	0.2514	0.5840	0.2162	4.40
C(6)	0.3635	0.6506	0.2335	4.42
C(7)	−0.0605	0.3634	0.1681	2.86
C(8)	−0.0622	0.3019	0.0992	3.39
C(9)	−0.2128	0.4137	0.1510	2.84
C(10)	−0.0152	0.3067	0.2447	3.01
C(11)	−0.1952	0.2433	0.0547	2.90
C(12)	−0.2119	0.2231	−0.0221	4.77
C(13)	−0.3352	0.1636	−0.0667	5.37
C(14)	−0.4255	0.1295	−0.0329	5.61
C(15)	−0.4065	0.1454	0.0459	4.78
C(16)	−0.2882	0.2062	0.0893	3.88
C(17)	−0.2589	0.4879	0.0943	3.15
C(18)	−0.2006	0.4965	0.0343	3.76
C(19)	−0.2604	0.5683	−0.0208	5.10
C(20)	−0.3792	0.6331	−0.0192	5.34
C(21)	−0.4289	0.6206	0.0414	4.91
C(22)	−0.3743	0.5475	0.0980	4.09
C(23)	0.0285	0.3534	0.3211	3.61
C(24)	0.0095	0.4513	0.3269	3.96
C(25)	0.0557	0.4929	0.4031	4.80
C(26)	0.1236	0.4354	0.4664	4.88
C(27)	0.1453	0.3390	0.4596	4.63
C(28)	0.0971	0.2948	0.3856	4.22
N(1)	0.1764	0.4138	0.2153	
N(2)	0.0448	0.4452	0.1764	
O(1)	0.0440	0.2990	0.0825	
O(2)	−0.2829	0.3858	0.1877	
O(3)	−0.0106	0.2230	0.2389	
Br	0.6654	0.7012	0.2960	

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	0.0079	0.0015	0.0036	0.0015	0.0032	−0.0002
N(2)	0.0090	0.0042	0.0021	−0.0019	0.0031	−0.0004
O(1)	0.0118	0.0068	0.0044	−0.0049	0.0069	−0.0043
O(2)	0.0101	0.0059	0.0039	0.0004	0.0066	0.0009
O(3)	0.0142	0.0049	0.0033	0.0019	0.0020	0.0006
Br	0.0137	0.0066	0.0084	−0.0100	0.0050	−0.0011

Table III. Summary of Bond Lengths and Interatomic Distances between Atoms Potentially Bonding during Rearrangements

Atoms (numbering in Figure 1)	Distance, ±0.02 A
C–C aliphatic	1.51–1.58
C–C aromatic	1.35–1.50
C(8)–O(1), C(9)–O(2), C(10)–O(3)	1.20
C(4)–N(1)	1.46
C(7)–N(2)	1.53
N(1)–N(2)	1.30
C(10)–N(1)	2.63
C(10)–O(2)	2.69
C(8)–O(3)	2.69
C(8)–N(1)	2.99
C(10)–O(1)	3.28
C(8)–O(2)	3.39
C(9)–O(3)	3.40
C(9)–N(1)	3.56
C(9)–O(1)	3.61

It will be seen that there is revealed no clearly defined preference for migration of an acyl group from carbon atom C(7) to an oxygen or to a nitrogen atom. No distances of less than 4 A are found between carbon and oxygen or carbon and nitrogen atoms in different molecules, a circumstance which argues against the point of view that intermolecular reaction though not found in solution occurs in the crystal because of the close proximity of appropriate atoms of neighboring molecules.

The Solid-State Rearrangement of the *p*-Bromobenzeneazo Compound IV. A layer of crystals of IV heated at 105° on a microscope hot stage appeared to turn from the original orange-yellow to bright red, the color of the enol benzoate V. When the temperature was raised to 145° the crystals became cream white as would be expected with the formation of hydrazone VI. Crystals of the azo compound IV, triclinic parallelepipeds with sides not more than 500 × 300 × 200 μ in length, obtained from diethyl ether were observed through a microscope with 100× magnification on a hot stage maintained at a temperature between 105 and 115°, the temperature being controlled to ±3° or better. Viewed by transmitted light either with or without crossed polaroid filters the orange-yellow crystal was seen to become opaque as reaction proceeded. This change did not occur uniformly over the surface of the crystal, however. Instead tiny dark veins appeared throughout much or all of the crystal, but a region of great disorientation began to develop in a limited area and gradually spread throughout the crystal. Frequently the region where reaction began most rapidly was a region with quite readily visible initial defects. The reaction generally appeared to spread most rapidly in a direction perpendicular to the long axis of the crystal and then across the length of the crystal. Viewed through the microscope by reflected light, the opaque region was seen to be the color of the red enol benzoate. Shortly after heating began white whiskers could be seen to grow on the vertical sides of the crystal and after several hours at 105° the crystals when viewed by reflected light appeared the bright red color of the enol benzoate V but with patches of white interspersed. The whiskers were separated and shown by their melting point behavior to be the white hydrazone VI. This compound, unlike its two isomers IV and V, was shown to undergo sublimation to an extent visible under the microscope at 105° and more seriously at 145°. Throughout these rearrangements there was no sign of melting or even softening or sintering, and at the end of the reaction crystal faces still clearly corresponded to those present initially although they were somewhat pitted and coated with small pockets of the white hydrazone VI. A further point was that different crystals or even different regions of the same crystal clearly varied greatly in the time required for rearrangement to be observed. Even after 5 hr at 105° there appeared to be a significant amount of starting material present, an observation confirmed by chemical analysis to be discussed. That the rearrangement was not beginning at the surface of the crystal and developing inward was suggested by careful examination of pictures taken at regular times during the rearrangement and by time-lapse motion pictures. It was confirmed by carrying out the rearrangement with finely ground azo compound IV which showed no apparent increase in the rate of development of the red color.

X-Ray diffraction techniques were also employed to elicit more detailed information about the retention or loss of order during reaction. When rearrangement of the powdered IV was carried out in a capillary by

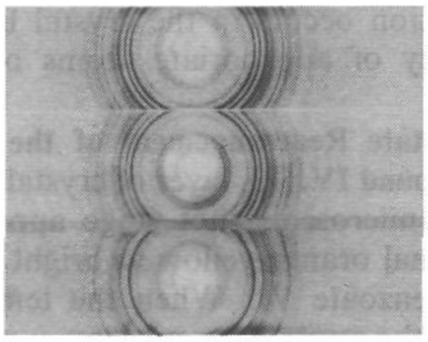

Figure 2. X-Ray powder patterns of the hydrazone VI: top, product of the solid-state reaction; center, VI recrystallized from methanol and heated at 210° for 30 min; bottom, VI recrystallized from methanol.

heating slowly (about 1°/min) to 160° the sample underwent the characteristic color change, yellow → red → cream white, with no sign of melting. A Debye–Scherrer powder pattern was recorded using nickel-filtered Cu Kα radiation. There was obtained a well-defined powder pattern different from that of either the starting material IV or the authentic hydrazone VI obtained by recrystallization from methanol. This was, in fact, the powder pattern of the hydrazone VI in a second crystalline form as was demonstrated by heating VI, obtained by recrystallization, at 210° for 0.5 hr; a pattern identical with that of the white solid-state reaction product was obtained as is shown in Figure 2. Unfortunately the volatility of VI revealed under the microscope suggests that no conclusion can be drawn concerning the orientation of molecules of VI as initially formed in the rearrangement. A second experiment was carried out with IV which had been powdered and pressed into a recessed brass sample holder. Traces were made with a General Electric diffractometer using nickel-filtered Cu Kα radiation after periods of heating. Peaks associated with the starting material diminished in intensity without appreciable broadening and were replaced by sharp peaks associated with the white hydrazone VI. A broad band of low intensity was observed to build up in the region $2\theta = 15\text{–}26°$, possibly owing to enol benzoate II, and then to disappear at the end of the reaction when the red color had disappeared and the powder appeared uniformly cream white. A prismatic single crystal of the azo compound I in a glass capillary was aligned in a Buerger precession camera and the *hk*0 net of the reciprocal lattice photographed with zirconium-filtered Mo Kα radiation. A stream of hot nitrogen gas was then directed into the capillary to induce rearrangement until the color was deep red. The reciprocal lattice net was again photographed and found to give only three diffuse rings with no areas of enhanced intensity. It is concluded that there was little orientation of product along the *b* crystallographic axis of the starting material.

Microscopic examination of crystals of the yellow azo compound IV undergoing reaction indicated that the rate of rearrangement varied widely from one crystal to the next. This suggested the desirability of studying the velocities of formation and ratios of products of individual crystals rather than as averages of the behavior of large numbers of crystals. Since the individual crystals weighed only 0.05–0.15 mg, product analyses were carried out by separating the starting material and products with thin layer chromatography and using ultraviolet spectroscopy to measure amounts of material in the separated spots. The results are presented in Table IV. Pairs of crystals which were judged, from the change in color and the amount of disorder which had been introduced, to have undergone rearrangement to about the same extent are compared.

Table IV. Chemical Behavior of Single Crystals of the Bromo Azo Compound IV on Heating

Time, hr (temp, °C)	Wt of initial crystal, mg	Appearance when analyzed	% reaction	Ratio of enol benzoate V to hydrazone VI
3 (105)	0.07 ± 0.01	Orange-red	23	0.96
	0.125		22	1.02
3 (105)	0.10	Bright red, opaque	66	0.82
	0.145		79	0.85
5 (105)	0.125	Deep red, very fractured, whiskers clearly visible	73	0.89
	0.09		91	0.86
...[a]	0.09	Cream white	100	0.00

[a] Heated 5 hr at 105° followed by 2 hr at 145°.

The results suggest that visual observation provides a fairly reliable estimate of the extent of reaction. More important is the conclusion that the ratios of enol benzoate:hydrazone did not vary appreciably from crystal to crystal. The values of the ratio after 66–79% reaction 0.82–0.85, are sufficiently different from the value of 1.05 measured in dioxane solution at 59 ± 2° to suggest that there may be some control of the products by carrying out the reactions in the solid state rather than solution. However, the accuracy of these values is not sufficient to allow much confidence in such a small difference. It cannot be decided at present whether the ratio of products is actually falling from 0.96–1.02 after 20% reaction to 0.82–0.85 after 80% reaction as the data in Table IV suggest, or whether the difference is simply a reflection of greater error in the values measured early in the reaction when relatively little of the products had accumulated to be analyzed.

Discussion

Isomerization reactions in molecular crystals have been reviewed by Morawetz.[8a] There seems to be little information about such reactions except the observation[8a] that their rates are characteristically much slower (10^3–10^4) than the corresponding reactions in solution. The great similarity, at least in a formal sense, of such processes to simple phase transitions of molecular crystals is apparent, and it is of interest that 31 years ago Hartshorne, Walters, and Williams[18] wrote, "The kinetics of reactions in the solid state have recently attracted considerable attention .... The theoretical approach to the subject would be facilitated if more data were available regarding the simplest type of reaction in the solid state, *viz.* the type solid$_1$ = solid$_2$, important examples of which are the transformations of polymorphic solids." This statement is as true today as it was then. A careful study of the

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[18] N. H. Hartshorne, G. S. Walters, and W. O. M. Williams, *J. Chem. Soc.*, 1860 (1935).

transition of monocrystal–monocrystal interconversion of α- and β-*p*-dichlorobenzene[19] has produced results which are highly relevant to the present study. The transition begins at defect sites, in general visible under the microscope. The most perfect crystals fail to undergo transition even well above the transition temperature. The polymorphic transition can be stimulated by the artificial creation of a defect in those crystals too perfect to undergo the change otherwise. The crystals of azo compounds I and IV employed in this study were undoubtedly less perfect than those used for the study of phase transitions.[19] Visual observation suggested, however, that as in the case of the polymorphic transition those crystals which were most perfect underwent reaction slowest and that rearrangement originated at visible defect sites and spread to other areas of the crystal. It may be recalled that grinding did little to accelerate the rearrangements so that internal defects and not added surface area seem to be important. A comparison of the rates of rearrangement of single crystals of the azo compound I with the rates estimated for solutions shows that the retardation in the crystal is by a factor of 100–400. However it is likely that these are simply minimum values and that the difference for sufficiently perfect crystals might approach infinity.

An attractive method of introducing defects into the crystal appears to be that of crystallizing in a solvent which is incorporated into the crystal lattice and then diffused out before rearrangement occurs. Thus, the yellow azo compound I, when recrystallized from chloroform, gave crystals containing the solvent which diffused out on standing. Preliminary work suggests that such desolvated crystals rearrange more rapidly and may give different product ratios than more perfect crystals. Work is being continued on this aspect of the rearrangement.

Experimental Section[20]

***p*-Bromobenzeneazotribenzoylmethane**[3] (IV) was prepared by a method analogous to that which had been previously employed[4] for related compounds. *p*-Bromobenzenediazonium fluoroborate[21] from 8.25 g (0.048 mole) of amine was added together with 38 g of sodium acetate in 200 ml of water at 0° and pH 8–9 to aqueous tribenzoylmethane anion from 11.8 g (0.036 mole) of tribenzoylmethane and 11.8 g of potassium carbonate in 1200 ml of ethyl acetate, followed by extraction of the anion into water. The product IV was extracted with a total of 1500 ml of ether after 5 min at 0° and the ether reduced to 20 ml on a rotary evaporator under reduced pressure. Filtration gave 5.43 g (38% based on the unrecovered tribenzoylmethane; 4.11 g of tribenzoylmethane was recovered by evaporation of the ethyl acetate solution above). Recrystallization from large amounts of ether between 25 and 0° or from benzene–hexane mixtures gave solvent-free crystals which when heated on a Kofler hot stage turn orange-red at 130–140°, lighten to an off-white at 160–165°, and melt at 227–228° (lit.[3] mp 130–135° on rapid heating).

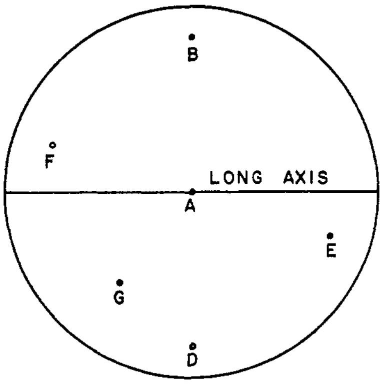

Figure 3. Stereographic projection of bromo azo triketone VI recrystallized from ether.

The infrared spectrum in methylene chloride solution showed a strong absorption at 1672 cm^{-1} with a shouder at 1700 and a sharp medium absorption at 1598 cm^{-1}. The ultraviolet-visible spectrum in methylene chloride solution showed $\lambda_{\max}$ 256 mμ (ϵ 30,000), 425 (378), sh 295 (19,000). Crystals employed for the rearrangement, purified by recrystallization from ether, had the same X-ray powder pattern as those recrystallized from benzene–hexane. A stereographic projection based on average angles for three crystals is shown in Figure 3.

Anal. Calcd for $C_{28}H_{19}BrN_2O_3$: C, 65.8; H, 3.7; N, 5.5; Br, 15.6. Found: C, 65.7; H, 3.6; N, 5.5; Br, 16.0.

α-*p*-Bromobenzeneazo-β-benzoyloxybenzalacetophenone (V). The azo triketo compound IV (1.5 g, 0.003 mole) in 12 ml of freshly purified dioxane was held at 57 ± 2° for 11 hr. Evaporation of the solvent with a rotary evaporator gave initially white solid which was removed by successive filtrations. The solid remaining after evaporation to dryness was treated with a small amount of dry ether which preferentially dissolved the red enol benzoate V; evaporation gave 225 mg of red oil which solidified in a few hours. After chromatography on a short Florosil column, recrystallization was carried out by dissolving the solid in a small amount of ether, adding hexane until the solution was cloudy, and cooling in a refrigerator. There was obtained 125 mg of V as fine red needles. The infrared spectrum (methylene chloride) showed strong absorption at 1746, 1678, and 1237 with a sharp band of medium intensity at 1455 cm^{-1}. The ultraviolet-visible spectrum (methylene chloride) showed $\lambda_{\max}$ 245 mμ (ϵ 33,200), 359 mμ (ϵ 26,500).

Anal. Calcd for $C_{28}H_{19}BrN_2O_3$: C, 65.8; H, 3.7; N, 5.5. Found: C, 65.8; H, 3.9; N, 5.3.

Diphenyl Triketone *sym*-Benzoyl-*p*-bromophenylhydrazone (VI), mp 227–228° (lit.[3] mp 220–221°) after recrystallization from methanol, could be prepared in nearly 100% yield by heating solid azo triketone III to 165° for 30–40 min. The infrared spectrum in methylene chloride showed strong absorption at 1680 with a shoulder at 1650 cm^{-1}. The ultraviolet-visible spectrum in methylene chloride showed $\lambda_{\max}$ 265 mμ (ϵ 23,800) and no absorption in the visible region.

Unit Cell, Space Group, and Density of Benzeneazotribenzoylmethane (I) and *p*-Bromobenzeneazotribenzoylmethane (IV). The parent compound I[4] crystallized from xylene–hexane as thin monoclinic plates with the *c* axis corresponding to the axis of elongation. The bromo derivative IV crystallized by slow evaporation from benzene–hexane with many well-developed faces, approximately equidimensional prisms (about 0.20 mm^3) with the corners removed by the development of diagonal faces and with principal axes lying along diagonals of the prism rather than parallel to the edges. Densities given in Table I were measured in each case by flotation in carbon tetrachloride–hexane. Unit cell dimensions (Table I) were measured employing crystals mounted in thin-walled (0.01 mm) Lindemann glass capillary tubes of 0.3-mm diameter with a Buerger precession camera (Charles Supper Co.).[14] In all cases Cu Kα radiation filtered through a thin nickel foil was employed with a film to crystal distance of 60.0 mm. Distances on the films were measured with an instrument manufactured by Charles Supper Co. In this and the other X-ray work discussed in this paper Ilford Industrial X-ray film, Type G, was employed

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(19) A. I. Kitaigorodskiy, Yu. V. Mnyukh, and Yu. G. Asadov, *J. Phys. Chem. Solids*, **26**, 463 (1965); Yu. V. Mnyukh, N. N. Petrotsavlov, and A. I. Kitaigorodskiy, *Dokl. Akad. Nauk SSSR*, **166**, 80 (1966); see also Yu. V. Mnyukh and M. A. Tseneva, *ibid.*, **162**, 326 (1965), and references cited in these papers for other studies of phase transitions in molecular crystals.

(20) All melting points are corrected. Infrared spectra were recorded by Mr. Dick Johnson and his associates with a Perkin-Elmer Model 521 spectrophotometer. Ultraviolet-visible spectra were obtained with a Bausch and Lomb Spectronic 505 instrument. Microanalyses were performed by Mr. J. Nemeth and his associates in the University of Illinois microanalytical laboratory.

A table of observed and calculated structure factors, the Patterson vector map and other X-ray data together with the infrared and other spectra are available in the Ph.D. Thesis of R. T. P. available from University Microfilms, Ann Arbor, Mich.

(21) J. J. Norman, *Can. J. Chem.*, **40**, 2023 (1962).

with processing in Kodak X-ray developer and fixed. The $0kl$ and $h0l$ nets of one crystal of IV aligned along c^* were photographed and the $hk0$ and $0kl$ nets of another aligned along b.* The space group was identified as P2$_1$/c by the systematic absences of $h0l$ reflections when l was odd and $0k0$ reflections when k was odd in precession photographs of levels $0kl$, $h0l$, $h1l$, $h2l$, $1kl$, $2kl$, and equiinclination Weissenberg photographs of levels $h0l$ through $h8l$.

Collection of Intensity Data. Precession photographs were obtained with a single crystal of bromo azo triketone IV approximately 0.25 × 0.28 × 0.32 mm mounted in a thin-walled (0.01 mm) Lindemann glass capillary 0.3 mm in diameter and aligned along the c^* axis. Intensity data were collected on the $0kl$ reciprocal lattice plane from photographs with exposures of from 5 min to 18 hr using nickel-filtered Cu Kα radiation, with the X-ray tube at 35 kv and 20 ma. Three-dimensional intensity data were obtained with a crystal 0.19 × 0.19 × 0.27 mm mounted in a thin-walled 0.5-mm Lindemann glass capillary alligned along the b axis in a Stoe Weissenberg X-ray goniometer by the multiple film equiinclination technique using nickel-filtered Cu Kα radiation. Data for levels $h0l$ through $k8l$ were obtained. Exposure times of 70 hr with the X-ray tube at 35 kv and 20 ma were employed and in addition for levels $h0l$ through $h4l$ 10-hr exposures were made. Four films were employed per multiple film pack. Intensities were measured with a modified Nonius microdensitometer by the method of Pfluger and Hon.[22]

Three-Dimensional Patterson Vector Map. Interlayer scaling of the three-dimensional equiinclination Weissenberg intensity data was achieved by reference to the $0kl$ precession intensity data previously mentioned. The intensity data for layers $h0l$ through $h8l$ (1303 reflections) were corrected for Lorentz polarization effects and for variations due to spot elongation on upper level photographs.[23] A three-dimensional Patterson vector map was computed in 50 sections along the y axis, the grid for each section consisting of units of 0.02 fractional cell units along x and 0.01 unit along z. A consistent set of bromine–bromine vectors could then be unambiguously chosen. The calculated expected height of the bromine–bromine vector in section $y = {}^1/_2$ was of the order of 900 whereas the observed value was 400 due to abnormally high thermal motion of the bromine atom. Bromine–bromine vectors, consistent with the assigned bromine coordinates, were found in the correct positions on the map, and in the right relative heights; they accounted for the eight most intense peaks in the map.

Trial Electron Density Maps and Three-Dimensional Least-Squares Refinement. A three-dimensional electron density map phased on bromine alone (assigned an arbitrary isotropic temperature factor of 2.0 A^2) was calculated using all 1303 observed reflections and gave on analysis assignment of positions of seventeen atoms; these results were used to calculate a new electron density map. This iterative procedure, with the positions of electron density maxima estimated by the method of Booth[24] and employing arbitrarily assigned isotropic temperature factors of 4.0 A,^{2} was continued until all 34 atomic positions were estimated. The coordinates so obtained were used to calculate a new set of structure factors and a structure factor program of Pfluger and Hon[22] used to correct the interlayer scaling. Full-matrix least-squares refinement of the structure was carried out using a program of Gantzel, Sparks, and Trueblood.[25] Two cycles were carried out in which only atomic positional parameters were allowed to vary with an arbitrary isotropic temperature factor of 4.0 A^2 assigned to all atoms. After three more cycles in which isotropic thermal parameters were allowed to vary, the high isotropic parameter of 6.33 A^2 obtained for bromine suggested the desirability of introducing anisotropic temperature factors for the bromine atom in the form

$$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

Two more cycles in which positional coordinates and anisotropic thermal parameters for the bromine atom were allowed to vary gave a drop of R from 16.7 to 10.9%. Two further cycles with anisotropic temperature factors assigned to both nitrogen and oxygen atoms gave a decrease of R only to 9.9%. Two final cycles in which all parameters were allowed to vary brought the R value to 9.8% with all 1303 reflections weighted equally. Final atomic coordinates and thermal parameters are presented in Table II.[26] The positional standard deviations were estimated from the diagonal elements of the normal equation matrix. For the C, N, and O atoms the average esd is 0.02 A.

Studies of the Rearrangement of Bromo Azo Triketone IV by X-Ray Techniques. The $hk0$ net of the reciprocal lattice of a prismatic single crystal of azo compound IV in a Lindemann glass capillary aligned by standard techniques along the a axis was photographed with a Buerger precession camera using zirconium-filtered Mo Kα radiation. The solid-state rearrangement was then effected with a stream of heated nitrogen gas directed onto the capillary which held the crystal. When a deep red color developed heating was stopped, and the reciprocal lattice net rephotographed showed only three diffuse rings with no areas of enhanced intensity.

A Debye–Scherrer powder pattern of bromo azo compound IV was recorded using nickel-filtered Cu Kα radiation. The sample was then heated on the hot stage of a microscope to 160°. The powder pattern of the off-white product was sharp and quite distinct from either the starting material or hydrazone VI crystallized from methanol. However, the recrystallized hydrazone VI when heated to 210° for 0.5 hr showed a powder pattern identical with that of the solid-state rearrangement product as shown in Figure 2. An experiment in which successive tracings of the pattern of the heated powder were made with a General Electric diffractometer and nickel-filtered Cu Kα radiation showed that the lines of the starting material IV diminished without broadening appreciably as the sharp lines of the hydrazone VI built up. At the stage corresponding to the formation of a deep red color there was a broadened region over the range of $2\theta = 15$–$26°$, possibly due to the enol benzoate V.

Use of Quantitative Chemical Methods to Follow the Solid-State Rearrangement of Bromo Azo Triketone IV. The rearrangement of single crystals weighing 0.06–0.145 mg was carried out on a Kofler hot stage with the temperature maintained at 105 ± 2° unless otherwise specified. Samples were weighed on a precision micro-torque balance with an estimated precision of ±0.01 mg. The crystal was dissolved in 10–15 μl of methylene chloride which had been dried and stored over Linde 4A molecular sieves and spotted on a strip of Eastman Chromatogram (Type K301R). The chromatogram was developed in 90:10 benzene–hexane. This procedure separated the C-azo compound IV and enol benzoate V from the hydrazone VI but not from each other. The chromatogram was dried, and the spots were outlined under ultraviolet light, cut out with scissors, extracted with methylene chloride, and diluted to 5.0 ml. Absorbances at 295 and 359 mμ were used to determine IV and V and at 265 mμ to determine the amount of hydrazone VI. Determinations of complete spectra were in agreement in test cases with those anticipated for these compounds. No other products were observed. Analysis of mixtures containing from 0.01 to 0.18 mg of the three substances gave results which suggested that the limiting factor was the error in weighing of the smallest samples (estimated to be ±0.01 mg). Results are presented in Table IV.

Duplicate reactions were carried out in purified[26] dioxane solution (0.05 M) at 59 ± 2°, the same analytical method being employed. Plots of ln (A_0/A) *vs.* time gave first-order plots for loss of starting material with $k_1 = 6 \times 10^{-5}$ and 7×10^{-5} sec^{-1} in agreement with the value of 8×10^{-5} sec^{-1} calculated from the unsubstituted compound I studied previously[4] employing values of 0.23 for $\sigma_{p\text{-Br}}$ and of +1.6 for ρ.[4] The average value of the ratio of enol benzoate:hydrazone was 1.05. Extrapolation of the rate constant to 105°, the temperature where the solid reaction was carried out, gave (using a value of 27 kcal/mole for E_a) $k_1 = 10^{-2}$ sec^{-1}.

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[22] C. E. Pfluger and P. K. Hon, unpublished work; P. K. Hon, Ph.D. Thesis, University of Illinois, 1964.

[23] D. C. Phillips, *Acta Cryst.*, 7, 746 (1954); **9**, 819 (1956).

[24] A. D. Booth, "Fourier Technique in X-Ray Organic Structure Analysis," The University Press, Cambridge, 1948, p 62.

[25] P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, ACA Computer Program No. 317, UCLALS 1.

[26] Observed and calculated structure factors and other data are available in the thesis of R. T. P.[1]