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Crystal Structure of *p*-Bromobenzylideneacetone

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The topochemical studies on the solid-state photodimerization of *trans*-cinnamic acid and its derivatives by Schmidt *et al.* have disclosed a correlation between crystal structure and photochemical behavior;[1] the dimerization takes place to form a cyclobutane ring between the carbon–carbon double bonds separated by no more than 4.1 Å, while no photoreaction occurs if the separation is more than 4.7 Å.

We found that benzylideneacetone, one of acyclic α,β-unsaturated ketones, readily yielded a photodimer in a solid state.[2] It may be interesting to see whether Schmidt's conclusion is also valid in this case. For convenience of X-ray anaylsis the *p*-bromo derivative was prepared, and examined for the photodimerization. The present paper will deal with the crystal structure of *p*-bromo-*trans*-benzylideneacetone in relation with photochemical reaction.

Experimental

p-Bromo-*trans*-benzylideneacetone was prepared by condensation of *p*-bromobenzaldehyde with acetone. Colorless tabular crystals, with well-developed (100), were obtained by recrystallization from acetone.

Photochemical Reaction. The solid-state ultraviolet irradiation (with a 125w high pressure mercury lamp) of the *p*-bromobenzylideneacetone for 12 days gave a dimer as a main product (48% yield, estimated from NMR data) and *cis*-benzylideneacetone (20%). The analytical and spectrometric data of the dimer are shown below; Found: C, 53.13; H, 4.03%, Calcd for $C_{20}H_{18}O_2Br_2$: C, 53.35; H, 4.02%. IR: ν_{max} 1707 cm^{-1} (C=O), UV: λ_{max} 261 nm (ε 540), NMR (100MHz): δ^{CDCl_3} 1.67 (s, 6H), 3.85 (q, J=11.0, 7.4 Hz, 2H), 4.56 (q, J=11.0, 7.4 Hz, 2H) and 7.37 (m, 8H). The mass spectrum showed a parent peak at m/e 448 and very strong peaks at 224 ($M^+/2$) and 209 ($M^+/2$—Me). These spectroscopic data well correspond to those of non-substituted benzylideneacetone. Therefore, the same conclusion can be drawn that the dimer is a centrosymmetric cyclobutane derivative.[2]

Crystallographic Data. Preliminary photographs taken with Cu$K\alpha$ radiation gave the crystallographic data as below: *p*-Bromobenzylideneacetone, $C_{10}H_9OBr$, M.W.: 225, mp 84°C, monoclinic: a=10.79, b=14.18, c=6.2 Å, β=91.2°, U=947.7 Å^3, Dm=1.59 g·cm^{-3}, Dx=1.59 g·cm^{-3}, Z=4. μ (Cu$K\alpha$)=61.4 cm^{-1}. Absent spectra: ($h0l$) when l is odd, ($0k0$) when k is odd, Space group is $P2_1/c$.

Three-dimensional intensity data were collected on multiple-film equi-inclination Weissenberg photographs taken with Cu$K\alpha$ radiation. Layer lines of zero to ten around the b axis and zero to four around the c axis were recorded. Measurement of the intensities was made by visual comparison with the standard intensity scale. Lorentz and polarization corrections were applied in the usual way and the structure factors obtained were put on a common scale by comparing those of the equivalent reflections appearing on different layers.

Structure Determination

The crystal structure was determined by the heavy atom method. Approximate coordinates of the bromine atom were derived from three-dimen-

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[1] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 1966.

[2] N. Sugiyama, K. Yamada, K. Sugiyama and H. Kataoka, *Nippon Kagaku Zasshi*, **88**, 769 (1967).

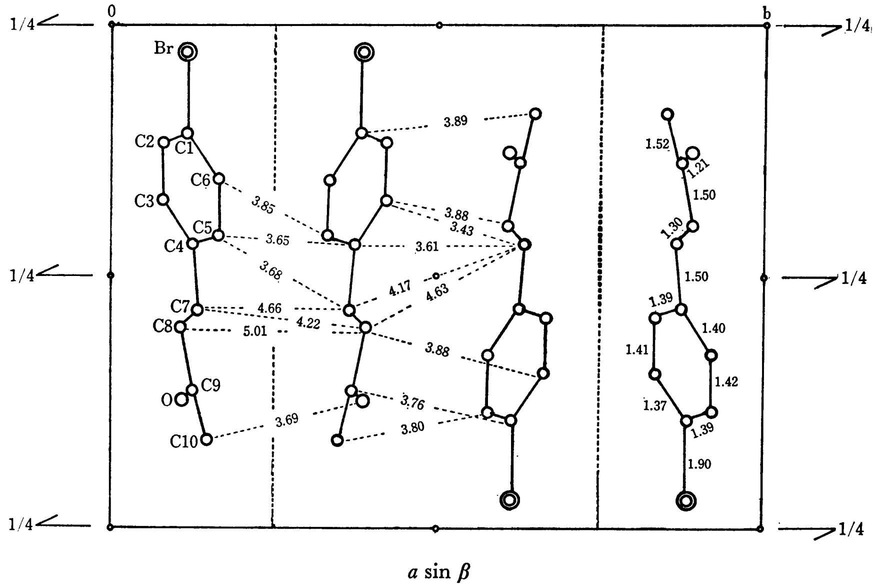

Fig. 1. Arrangement of molecules projected along [001].

Table 1. Final atomic coordinates and temperature factors

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

Atom	x/a	y/b	z/c	B(Å^2)
Br	0.0496	0.1158	1.2657	*
O	0.7502	0.1074	0.4248	5.83
C(1)	0.2108	0.1177	1.1492	3.68
C(2)	0.2280	0.0793	0.9455	3.26
C(3)	0.3476	0.0797	0.8529	3.58
C(4)	0.4446	0.1202	0.9759	3.14
C(5)	0.4241	0.1581	1.1780	3.41
C(6)	0.3054	0.1572	1.2676	3.40
C(7)	0.5736	0.1274	0.8935	3.33
C(8)	0.6049	0.1075	0.6977	4.03
C(9)	0.7325	0.1229	0.6133	4.13
C(10)	0.8376	0.1514	0.7659	4.76

* $B_{11}=0.00765$, $B_{22}=0.00826$, $B_{33}=0.04249$, $B_{12}=0.00168$, $B_{13}=0.00635$, $B_{23}=-0.00204$.

sional sharpened Patterson function without ambiguity. The three-dimensional Fourier synthesis, with the phases of bromine atom only, revealed all the non-hydrogen atoms. At this stage, $R=0.21$. The refinement of the structural parameters was carried out by the method of least-squares, using all the 1956 observed reflections. Three cycles of block-diagonal matrix refinement reduced the R to 0.148, only the bromine atom being treated as anisotropic. The final atomic coordinates and temperature factors are listed in Table 1.

Discussion

The bond lengths, angles and intermolecular contacts obtained show no unusual value in view of e. s. d. 's. The nearest carbon–carbon double bonds are those related by center of symmetry, at a center-to-center distance of 4.63 Å, and those by glide-plane at a center-to-center distance of 4.84 Å. In the latter pair, the molecules are somewhat farther and not parallel with each other. Therefore, dimerization of the latter pair may be less probable, according to the least motion principle,[3] which describes that the most favorable elementary reactions should be those involving the least change in atomic position and electronic configuration. On the other hand, the dimerization between the former pair might be more favorable and this is compatible with the conclusion that the main product of the solid-state photochemical reaction of *p*-bromobenzylideneacetone is a centrosymmetric dimer.[2]

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[3] F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).