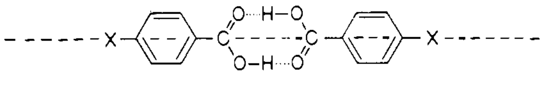


$X = OCH_3, CH_3, Cl$

Figure 2. Para-substituted benzoic acids. (- - -) direction of the longitudinal axis and of the transition moment of the ET band.

the carbonyl carbon and the neighboring carbon atom as shown in Figure 1.[7]

We have corroborated the latter assignment using dichroic ratio values of three para-substituted benzoic acids (Table II). Previously we have shown that benzoic acids incorporated in stretched polyethylene films are completely dimeric. Using the same reasoning as previously, we deduce that the three acids have the same fractions of orientation and that their longitudinal axis is in the plane of the molecules (Figure 2). These assumptions allow the use of the differences in α values ($\Delta\alpha$) between two para-substituted esters for the corresponding acids. Solving eq 1 for the acids, using $\Delta\alpha$ values of the esters, gives $f = 0.72$. Since, as shown in the Tables I and II, the calculated α's of the corresponding acids and esters are identical within experimental error, the longitudinal axes in both series of compounds have the same relations to the benzyloxy chromophores. Thus all α values in Tables I and II define the angles which the transition moments form with the axis passing through the carbonyl carbon and the neighboring carbon atom. However, when a particular band is composed of transitions having different polarizations the α's define merely their vectorial resultants.

From the data in Tables I and II the following may be seen: the shortest wavelength transition (A band)[8] has, in all compounds studied, similar values of "longitudinal" polarization.[9] At longer wavelengths, the para-substituted esters and acids exhibit an additional band having a "transversal" polarization.[9] Since both these bands are not well resolved, the actual $\mathbf{d}_0$ values of these bands may have smaller and larger values, respectively. In addition, it is not improbable that in other benzoic acids and esters the additional band is hidden below the A band.

Contrary to the case for A band, the polarizations of the B and C bands depend on the substituents in the benzene ring and their relative positions. It is to be pointed that the direction of polarization of the C band changes with vibronic states of this transition.

The knowledge of the direction of the transition moments enables the establishment of the rotameric conformation of benzyloxy groups also in other positions of a molecule, provided its f value is known.[10]

This may be exemplified by measurement of 17β-benzyloxyandrost-5-ene. We have established its fraction of orientation, f (0.37), by measurement of the $\mathbf{d}_0$ of 17β-cyclohexanoxy ketones **3** and **4** (1.64 and 2.14) and by substitution of these values into eq 1, remembering that $\alpha_3 + \alpha_4 = 60°$. This calculation gives us also the direction of the longitudinal axis of **3** and **4**. Assuming the same f and the same position of the longitudinal axis also in 17β-benzyloxyandrost-5-ene, and using the $\mathbf{d}_0$ value found for the B band of this compound (2.1), we have calculated the respective α.

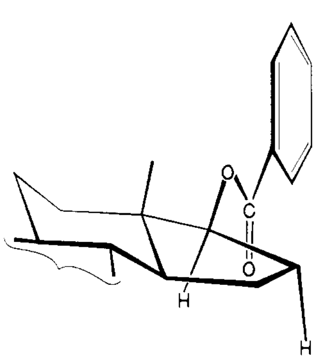
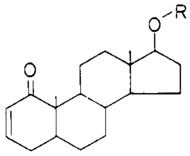
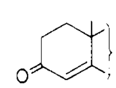


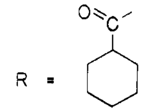
Figure 3. Conformation of the benzyloxy group in 17β-benzyloxyandrost-5-ene (only rings C and D are shown in the picture).



3



4



Knowing independently the direction of the transition moment in the coordinates of the chromophore and the position of the longitudinal axis in the coordinates of the steroid skeleton, we have established the rotameric conformation of the benzyloxy substituent which is shown in Figure 3.

Similar treatment may be used to distinguish between axial and equatorial esters.

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(7) In establishing this rotational conformation the values of the relevant bond angles were taken into consideration.

(8) (a) M. Ito, *J. Mol. Spectrosc.*, **4**, 144 (1960); (b) C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951); (c) H. E. Ungnade and R. W. Lamb, *J. Amer. Chem. Soc.*, **74**, 3789 (1952).

(9) Longitudinal and transversal polarizations are those which have dichroic ratios greater and smaller than 1.00, respectively.

(10) We have applied this method also to 3-benzyloxyandrostanes. In spite of a different fraction of orientation in these molecules, the same values of transition moments and of the conformation of the benzyloxy chromophore were obtained as in the analogous cholestane derivatives.

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Received September 16, 1970

The Alteration of Nuclear Magnetic Resonance Polarization in the Sensitized Photolysis of Benzoyl Peroxide[1]

Sir:

Nuclear magnetic resonance (nmr) emission and enhanced absorption were first reported 3 years ago. The polarizations could be produced in chemical reactions[2] as well as in photophysical processes.[3,4] In the much

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(1) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract ORGN 42.

(2) (a) J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch. A*, **22**, 1551 (1967); (b) J. Bargon and H. Fischer, *ibid.*, *A*, **22**, 1556 (1967); (c) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 1518 (1967); (d) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968); (e) A. R. Lepley, *J. Amer. Chem.Soc.*, **90**, 2710 (1968).

(3) G. Maier, U. Haeberlen, H. C. Wolf, and K. H. Hausser, *Phys. Lett. A*, **25**, 384 (1967).

(4) M. Cocivera, *J. Amer. Chem. Soc.*, **90**, 3261 (1968). The irradia-

Table I. Polarization of Benzene in the Photolysis of BPO[a]

Sensitizer	Triplet energy[b]	Fluorescence quantum yield	Solvent	Benzene spectrum[c]
None			Cyclohexane	E
None			Cyclohexane and 0.7 *M* benzene	E
None			Butyl acetate	E
None			Carbon tetrachloride	E[k]
Acetone	78	$<10^{-2}$ [b]	Acetone	A
Cyclohexanone	~78	$<10^{-2}$	Cyclohexanone	A
Acetophenone-d_5[d] (0.5 *M*)	74	~0[e]	Cyclohexane	A
Michler's ketone[f]	61	~0	Butyl acetate	A
2-Acetonaphthone[g]	59	$<10^{-2}$	Butyl acetate	A
1-Acetonaphthone[g]	56	$<10^{-2}$	Butyl acetate	N or small A
Benzil[g]	54	$<10^{-2}$	Butyl acetate	N
Biacetyl[g]	55	$<10^{-2}$	Butyl acetate	N
Triphenylene-d_{12}[g]	67	0.11[h]	Butyl acetate	E
Phenanthrene[g]	62	0.15[i]	Butyl acetate	E
Pyrene[f]	49	0.32[h]	Butyl acetate	E
Anthracene[g]	42 ($74T_2$)[j]	0.32[h]	Butyl acetate	E
Xanthone[g]	74	$<10^{-2}$	Butyl acetate	N
Benzophenone[g]	69	~0[e]	Butyl acetate	N
Acetophenone	74	~0[e]	Carbon tetrachloride	A[k]

[a] Solutions of BPO (0.02 *M*) in thin-walled Pyrex tubes were irradiated with a medium-pressure mercury-xenon lamp in the cavity of a 60-MHz spectrometer. [b] A. A. Lamola and N. J. Turro, *Tech. Org. Chem.*, **14**, 91,194 (1969). [c] A, enhanced absoption; E, emission; N, no polarization. [d] We thank Dr. A. A. Lamola for the generous gift of deuterated acetophenone. [e] See ref 15 (even the delayed fluorescence has a quantum yield of $<10^{-2}$; W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1970)). [f] Irradiated through a Corning 0-52 filter. [g] Irradiated through a Corning 0-54 filter. [h] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965. [i] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 310. [j] R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **90**, 213 (1968). [k] Chlorobenzene spectrum.

studied thermal[5] and photochemical[6] decomposition of benzoyl peroxide (BPO) in an nmr spectrometer, the benzene which is formed always gave an emission spectrum. We report the first example of an enhanced absorption of benzene produced in the spectrometer cavity, which occurred when certain triplet sensitizers were present. Therefore, the nature of the polarization is dependent on the multiplicity of the excited state of BPO involved in the primary photochemical step.

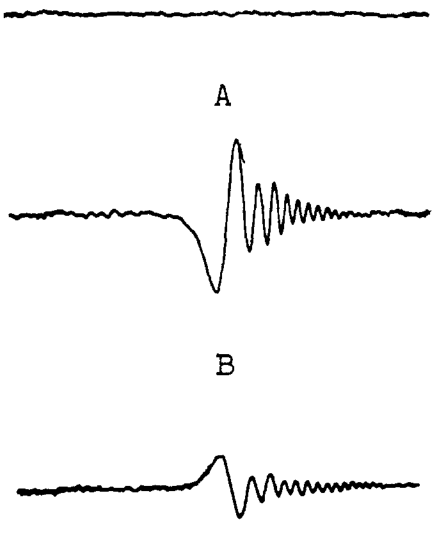
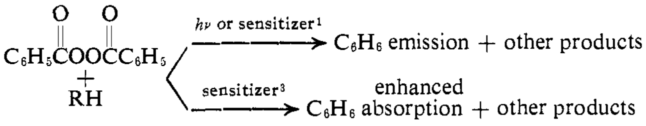


Figure 1. Fast-sweep nmr spectra of the phenyl region of 0.02 *M* solutions of BPO in cyclohexane: (A) no irradiation; (B) during irradiation; (C) during irradiation of solution also containing 0.5 *M* acetophenone-d_5.

Closs and Trifunac first made the important observation that a given product may exhibit a certain pattern of polarization or its exact opposite depending on the spin multiplicity of the radical-pair precursor.[7] However, they were required to use two different sources to generate the radical pairs of different multiplicities. In the present study there was only one source for both radical pairs and the nature of the sensitizer was the only difference in the experimental conditions.



$$C_6H_5\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}C_6H_5 + RH \xrightarrow{h\nu \text{ or sensitizer}^1} C_6H_6 \text{ emission} + \text{other products}$$

$$C_6H_5\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}C_6H_5 + RH \xrightarrow{\text{sensitizer}^3} \text{enhanced } C_6H_6 \text{ absorption} + \text{other products}$$

Walling and Gibian[8] found that all ketone sensitizers effective in the photodecomposition of BPO have a triplet energy of 59 kcal/mol or greater, while ketone sensitizers whose triplet energy is less than 55 kcal/mol were inactive. Correspondingly, we have found that enhanced absorption is observed only with sensitizers having a triplet energy of 59 kcal/mol or greater, *e.g.*, cyclohexanone, acetone, acetophenone, Michler's ketone [4,4′-bis(dimethylamino)benzophenone], and 2-acetonaphthone (Figure 1). Pyrex nmr tubes were always used and served as a light filter. (With quartz tubes nmr emission rather than enhanced absorption resulted since the BPO absorbed the light directly at the lower wavelengths.) No enhanced absorption

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tions in the present communication were conducted with the optical system devised by M. Cocivera.

(5) H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and references therein.

(6) M. Lehnig and H. Fischer, *Z. Naturforsch. A*, **24**, 1771 (1969).

(7) G. L. Closs and A. D. Trifunac, *J Amer. Chem. Soc.*, **91**, 4554 (1969).

(8) C. Walling and M. V. Gibian, *ibid.*, **87**, 4313 (1965).

was observed with sensitizers of less than 56 kcal/mol triplet energy such as benzil and biacetyl. 1-Acetonaphthone gave a very small enhanced absorption probably because it has a marginally sufficient triplet energy of 56 kcal/mol.

However, high triplet energy is not a sufficient condition for enhanced absorption as seen in Table I. All sensitizers having a fluorescence quantum yield greater than 10^{-2} (phenanthrene, triphenylene, anthracene, and pyrene) gave an emission signal regardless of their triplet energy. The unsensitized decomposition also gave an emission signal,[6] but Corning 0-54 or 0-52 filters could screen out essentially all the direct irradiation. The appreciable room-temperature fluorescence of the hydrocarbons indicates that they have a relatively large singlet yield. The aromatic hydrocarbon sensitization must involve, at least in part, singlet energy transfer. This is confirmed by the observation of fluorescence quenching of anthracene and triphenylene by BPO in the concentration range used in the nmr experiments. The Stern–Volmer quenching constants in butyl acetate for anthracene and triphenylene are 1×10^{10} l. mol^{-1} sec^{-1} and 2.4×10^{9} l. mol^{-1} sec^{-1}, respectively, *i.e.*, close to diffusion controlled. There are a number of other examples of reactions for which singlet sensitization by triphenylene,[9–13] anthracene,[11,13] phenanthrene,[12,13] and pyrene[9,11–13] is well established. Since the absorption of anthracene, triphenylene, and pyrene occurs at longer wavelengths than that of the BPO, a possible mechanism is charge-transfer complex formation between ground-state BPO and excited singlet sensitizer.[14]

When carbon tetrachloride was the solvent in the photodecomposition of BPO, chlorobenzene was the product obtained.[6] As in the case of benzene, nmr emission was observed on direct irradiation and enhanced absorption when a triplet sensitizer was used.

The reason that 2-acetonaphthone gave an enhanced absorption while equivalent concentrations of benzophenone and xanthone gave no polarization is probably related to the well-known difference in reactivity between ketones having π–π^* and those having n–π^* triplet states.[15] Ketones with n–π^* states, like benzophenone, undergo photoreductions very readily to produce radicals which may induce the decomposition of BPO. For example, in the photosensitized decomposition of BPO, differences in product ratios have been observed between 2-acetonaphthone and benzophenone.[16] Smith interpreted his results as an induced decomposition of BPO by benzophenone-derived ketyl radicals, but that ketyl radicals are not formed in the 2-acetonaphthone case.[17] It has been predicted by Kaptein that induced decomposition leads to no net polarization.[2d] To check this hypothesis the thermal decomposition of BPO was carried out in solvents which have been reported to promote induced decomposition.[18] In neither ethylene glycol monoethyl ether nor isopropyl alcohol was nmr emission observed at temperatures which normally result in strong emission, and in dioxane or ethylene glycol monoethyl ether acetate the emission was very weak.

We conclude that the polarization of benzene formed from the decomposition of BPO is directly related to the multiplicity of the excited state in the primary photodecomposition. Enhanced absorption results from the triplet-sensitized state which occurs only when three conditions are met: sufficient triplet energy, low fluorescence yield, and little photoreduction under the reaction conditions. Direct photolysis and singlet-sensitized photodecomposition result in nmr emission.[19]

Acknowledgment. We are grateful to Dr. Saul Meiboom and Mr. Richard C. Hewitt for their patience and guidance in the use of their specially modified 60-MHz nmr spectrometer, and we are indebted to Dr. Gary N. Taylor for very helpful discussions.

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(9) (a) P. de Mayo, J. P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (b) J. S. Swenton, T. V. Ikeler, and B. H. Williams, *Chem. Commun.*, 1263 (1969); (c) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969).

(10) A. B. Smith, III, and W. C. Agosta, *Chem. Commun.*, 4666 (1970).

(11) S. Murov and G. S. Hammond, *J. Phys. Chem.*, 72, 3797 (1968).

(12) F. D. Lewis and J. C. Dalton, *J. Amer. Chem. Soc.*, **91**, 5260 (1969).

(13) (a) P. D. Bartlett and P. S. Engel, *ibid.*, **90**, 2960 (1968); (b) P. S. Engel, *ibid.*, **91**, 6903 (1969).

(14) B. S. Soloman, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).

(15) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 75.

(16) W. F. Smith, Jr., *Tetrahedron*, **25**, 2071 (1969).

(17) With aliphatic solvents such as were used in the present study, hydrogen abstraction by the benzophenone triplet would occur even more readily.

(18) P. D. Bartlett and K. Nozaki, *J. Amer. Chem. Soc.*, **69**, 2299 (1947).

(19) Note Added in Proof. R. Kaptein, J. A. den Hollander, D. Antheunis, and L. J. Oosterhoff have studied similar systems and independently reached the same conclusion. We thank these authors for a preprint of their work.

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Received October 7, 1970

A Study of the $C_3H_7^+$ Ion by Ion Cyclotron Resonance Spectrometry

Sir:

The possible structures of $C_3H_7^+$ are of interest not only in mass spectroscopy[1] but also in solution chemistry,[2] radiolysis,[3] and in molecular orbital calculations.[4] A number of structures can be written for this rather simple cation including *n*-propyl, isopropyl, and various protonated propenes and cyclopropanes. Despite this variety, there is compelling evidence that the $C_3H_7^+$ ions formed from various alkanes in the mass spectrometer possess a common structure.[5] More recently, appearance potential measurements of $C_3H_7^+$ from propyl radicals show that two isomeric $C_3H_7^+$ ions exist at the threshold (presumably *n*- and isopropyl).[6] However, since these appearance potentials are nonadiabatic, there is some question as to how much smaller the adiabatic value is.[6] Appearance potentials of $C_3H_7^+$ from a variety of sources yield heats of

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(1) See W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 4745 (1968), and references cited therein.

(2) See G. J. Karabatsos, M. Anand, D. O. Rickter, and S. Meyerson, *ibid.*, **92**, 1254 (1970), and references cited therein.

(3) (a) P. Ausloos, R. E. Rebbert, and S. G. Lias, *ibid.*, **90**, 5031 (1968); (b) S. G. Lias, R. E. Rebbert, and P. Ausloos, *ibid.*, **92**, 6430 (1970).

(4) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); and references cited therein.

(5) H M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963, p 518.

(6) F. A. Elder, C. Giese, B. Steiner, and M. Inghram, *J. Chem. Phys.*, **36**, 3292 (1962); C. E. Melton and W. H. Hamill, *ibid.*, **41**, 3464 (1964).