Structure and Photochemistry of Matrix-isolated *o*-Phthalaldehyde

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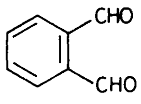
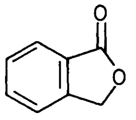
Two conformers, (*EZ*) and (*EE*), were observed in *o*-phthalaldehyde (**1**) isolated in nitrogen and argon matrices. The *E*-enol (**5*E***) generated upon photolysis (λ 313 nm) of the matrix-isolated (**1**) was stabilized and characterized by UV and IR absorption spectroscopy. Further irradiation of (**5*E***) resulted in intramolecular cyclization ($\lambda > 357$ nm) to phthalide (**2**) or fragmentation ($\lambda = 313$ nm) to carbon monoxide and benzaldehyde (**7**).

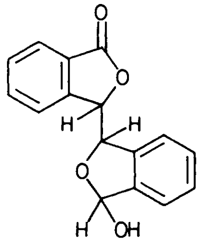
Photochemical transformations of *o*-phthalaldehyde (1) have been studied in several laboratories.[1-5] In general, it has been observed that the photolysis of (1) in solution leads to the formation of the phthalide (2) and an isomeric mixture of dimers (3). Relative yields of these products depend strongly upon the solvent employed. Various intermediates have been considered in the mechanistic discussions and the last contribution by Scaiano and co-workers[5] added important information to assist in the elucidation of the mechanism of room-temperature photolysis of (1) in solution. It has been reported that the phthalide (2) and the dimer (3) arise from the singlet-state reaction involving the cyclic enol (4) as an intermediate. The triplet state reaction leading to the mixture of enols (5*Z*) and (5*E*) *via* common biradical precursor does not seem to contribute to the formation of the stable photoproducts and the enols (5*Z*) and (5*E*) revert to (1) quite efficiently. It was also stated that the transient absorption observed at 390 nm in the laser flash photolysis experiments well resembles the steady-state spectrum of irradiated (1) in a methylcyclohexane glass at 77 K and both absorptions were assigned to (4).



(1)



(2)



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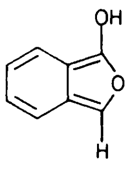

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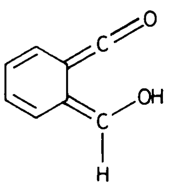
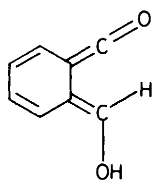


(5*Z*)



(5*E*)

Our contribution presents the results of the studies on the photochemical transformation of (1) under matrix-isolation conditions. The application of IR matrix-isolation spectroscopy,[6-8] which is characterized by high spectral resolution, allows us to analyse for primary and secondary photochemical reactions and to relate the spectral characteristics of starting material and photoproducts to specific structural featues. Preliminary communication from our laboratory[9] provided direct evidence for the stabilization of the photoenol (5*E*) in a nitrogen matrix. This paper extends these studies considering the problems related to conformational preferences and photochemical behaviour of matrix-isolated *o*-phthalaldehyde (1) and its primary photoproduct.

Experimental

Materials.—Chemicals used in these studies were purchased from POCh (Poland) and purified, if necessary, by standard laboratory procedures. Deuterium-labelled *o*-phthalaldehyde was prepared by the decomposition of deuteriated ω,ω,ω′,ω′,-tetrabromo-*o*-xylene in oleum (20%).[10] Labelled tetrabromo-*o*-xylene was obtained by isotope exchange with MeOD, carried out in sealed glass ampoules for 3 hours at 90 °C. Phthalide and *o*-phthalaldehyde were formed as side products. Tetrabromo-*o*-xylene was separated by crystallization and the labelling procedure was repeated until a satisfactory deuterium enrichment was achieved. Based upon analysis of the ^1H and ^2H NMR spectra (Bruker MSL 300) the following isotopic purity was observed in the sample of deuteriated *o*-phthalaldehyde used in the measurements: aldehydic hydrogens, 89%; ring hydrogens in 3,6-positions, 10%; ring hydrogens in 4,5-positions, 34%.

Nitrogen and argon gases were supplied by Gazy Techniczne (Poland) and purified by passing through low-temperature traps.

Sample Preparation.—A gaseous mixture of known amounts of the substrate vapour and matrix gas was deposited from a vacuum line (background pressure of $0.5–2 \times 10^{-5}$ Torr †) onto a caesium iodide or sapphire window mounted on the expander stage of a Spectrim (Cryogenic Technology) cryostat. The gas mixture was deposited at a flow rate of 50–70 μmol min^{-1} and the total amount deposited varied from 0.5 to 9 mmol. If the substrate pressure was very low, *i.e.* insufficient to prepare a gas mixture, a matrix gas was passed over a solid substrate placed in the thermostatted tube, connected to the deposition line behind the needle valve. In this method of deposition the matrix ratio (*M*/*R*) is not known and can only be estimated. Nitrogen and argon matrices were usually deposited at 20 K.

Irradiation and Measurements.—Photochemical reactions

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† 1 Torr ≈ 133.322 Pa.

Table 1. Observed vibrational frequencies (cm^{-1}) of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**).[a]

3 092w	1 599s[b]	1 160w
2 925m[b]	1 581s	1 102w
2 870w	1 492w	1 003w
2 852w	1 455w	860s
2 758m	1 405w	808s[b]
1 725s	1 391(sh)	766s[b]
1 708s[b]	1 308m	715w
1 695s	1 272m	657m
1 670w	1 200s[b]	627m
1 621w	1 193(sh)	430w

[a] *T* 15 K, *c* 9 mmol, *M*/*R* *ca.* 400. [b] Bands where a contribution from the photochemically less reactive species was evident.

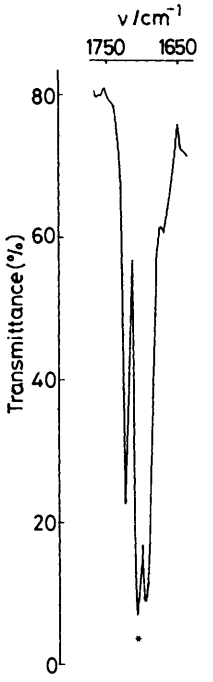


Figure 1. The carbonyl stretching region of the IR spectrum of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**) (*T* 15 K, *c* 9 mmol, *M*/*R* *ca.* 400). The asterisk indicates the band of the photochemically less reactive species.

were carried out with a high-pressure mercury lamp HBO-200 (Narva, GDR). Interference filters UV-KSIF (Zeiss Jena, GDR) and glass cut-off filters (Oriel) were used. IR spectra of matrix-isolated species were obtained with a Specord M-80 (Zeiss Jena, GDR) spectrophotometer working at resolution of 2 cm^{-1}. The band positions were calibrated with a polystyrene reference spectrum and the error of frequency reading was ±1 cm^{-1}. UV–visible absorption spectra were measured with a UV–VIS (Zeiss Jena, GDR) spectrophotometer with no baseline correction for light scattering caused by a matrix. The irradiation and measurements were performed at 15 K.

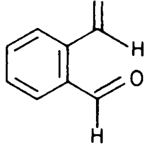
Results and Discussion

Structure of Matrix-isolated o-*Phthalaldehyde.*—Three different conformations, (*EZ*), (*EE*), and (*ZZ*), are feasible for (**1**). Rotational isomerism of (**1**) has been studied by a variety of methods,[11-13] but, surprisingly, IR spectroscopy has not been applied to this problem. It has been found that the conformer stability decreases in the following order: (**1***EZ*) > (**1***EE*) > (**1***ZZ*). As one could expect the stability of the (**1***ZZ*) rotamer is the lowest, due to the oxygen–oxygen electrostatic and steric repulsions, and its destabilization is about 20kJ mol^{-1} in comparison with (**1***EZ*).[13] Two other rotamers (**1***EZ*) and (**1***EE*) are close in energy and it has been shown from the ^{1}H NMR spectrum that both exist as an 87:13 mixture in carbon tetrachloride.

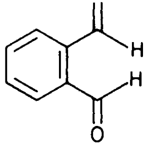
Table 2. Observed vibrational frequencies (cm^{-1}) assigned to the primary photoproduct of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**).[a]

3 650m	1 537w
2 110m	1 218m
2 097s	1 152w
2 085s	1 138m
1 638w	753m

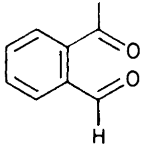
[a] *T* 15 K, *c* 9 mmol, *M*/*R* *ca.* 400.



(**1***EZ*)



(**1***EE*)



(**1***ZZ*)

It has been found that matrix-isolation spectroscopy can be applied to the analysis of the gas-phase conformational equilibria by a rapid quenching of conformational mixture during matrix formation.[14] In principle, this method should also be applicable to the *o*-phthalaldehyde. Observed vibrational frequencies of nitrogen-matrix-isolated (**1**) are tabulated (Table 1) and the carbonyl stretching region is shown in Figure 1. The three strong, relatively broad absorptions found suggest the presence of more than one conformer. Similar observation has been made for argon-matrix-isolated (**1**). All three bands represent monomeric species since the contribution from aggregates is negligible, as indicated by the spectra recorded for diluted matrices (*M*/*R* *ca.* 1 200). Neglecting the contribution from the (**1***ZZ*) rotamer and assuming that the gas-phase conformational mixture was quenched during the deposition, one would expect three bands in the carbonyl stretch region, two of them due to (**1***EZ*) and one due to the (**1***EE*) rotamer. We assign the band observed at 1 708 cm^{-1} to (**1***EE*) and the two bands observed at 1 725 and 1 695 cm^{-1} to (**1***EZ*). Among the two bands assigned to the (**1***EZ*) rotamer we believe that the band observed at lower frequency (1 695 cm^{-1}) is due to the carbonyl group facing the aldehydic hydrogen. Weak interactions due to hydrogen bonding can shift the C=O stretch of interacting group to lower frequency.[15] Additional support for an assignment of the carbonyl absorptions comes from the temperature-dependent measurements performed in non-polar solvents.[16] Also photochemical observations clearly indicated a serious difference in photochemical behaviour between the (**1***EZ*) and (**1***EE*) rotamers.

Nature of the Primary Photoproduct.—The photoproduct generated from the matrix-isolated (**1**) possesses a UV–visible spectrum (λ_{max} 390 nm) (Figure 2) indicative of an extended chromophore, and is consistent with the properties expected for the photoenol.[17] The spectrum appears to show vibrational structure with the frequency progression about 1 200 cm^{-1}. The IR spectrum of the new species seems to provide important arguments for the structural characterization. Vibrational frequencies of the photoproduct are tabulated (Table 2) and important fragments of its IR spectrum are presented in Figure

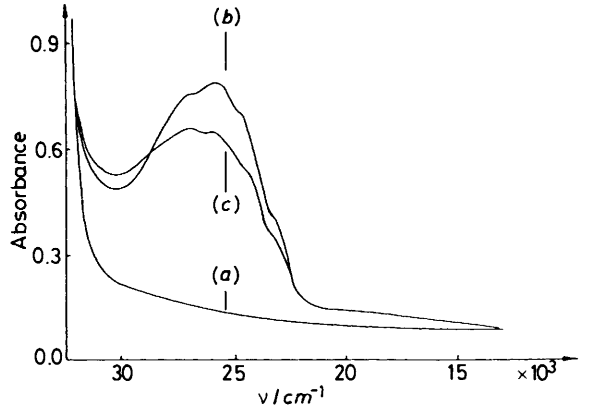


Figure 2. Electronic absorption spectrum of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**) (*T* 15 K, *c* 0.8 mmol, *M*/*R* *ca.* 400): (*a*) before irradiation; (*b*) after irradiation for 4 min through a 313 nm interference filter; (*c*) after irradiation through a 313 nm interference filter (for 4 min) and a 357 nm cut-off glass filter (for 12 min).

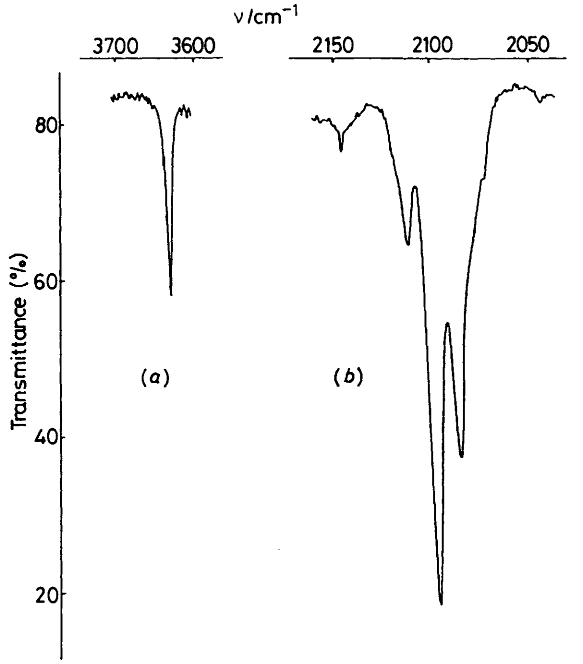


Figure 3. Expanded hydroxy (*a*) and ketene (*b*) stretching regions of the IR spectrum of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**) (*T* 15 K, *c* 9 mmol, *M*/*R* *ca.* 400). The sample was irradiated through a 313 nm interference filter for 6 min.

Table 3. Observed vibrational frequencies (cm^{-1}) assigned to the secondary photoproduct (λ > 357 nm) of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**).[a,b]

2 925m[c]	1 758(sh)	1 219m[c]
1 790(sh)	1 469w	1 063m
1 781m	1 361w	1 020w
1 768m	1 290m	742m[c]

[a] *T* 15 K, *c* 9 mmol, *M*/*R* *ca.* 400. [b] Observed vibrational frequencies of nitrogen-matrix-isolated phthalide (**2**) given as a reference: 2 960w, 2 925m, 2 858w, 1 805w, 1 791s, 1 780m, 1 769s, 1 759m, 1 622m, 1 469m, 1 456w, 1 362m, 1 315m, 1 295m, 1 288m, 1 219m, 1 198w, 1 107w, 1 063m, 1 042s, 1 020m, 1 011m, 740s, 681w, and 580w. [c] Absorptions superimposed on the bands observed in starting material or primary photoproduct.

3. The signal at 3 650 and the split signal in the vicinity of 2 100 cm^{-1}, shown in Figure 3, can be assigned to the O–H and C=C=O stretching vibrations, respectively. The evidence given above contains all the typical features to be expected for the photoenol. IR bands at 1 638 (C=C str.), 1 218 (OH bend), and 1 138 (CO str.) are also compatible with such an assignment. A cyclic enol (**4**) can be excluded from the discussion since the IR spectrum assigned to the photoproduct included a signal very characteristic of the ketene functionality, which is not present in (**4**). The single band characteristic of free O-H (ν 3 650 cm^{-1}) points towards a single photoenol, *i.e.* (**5***E*). The (*Z*)-enol (**5***Z*) would very likely form an intramolecular hydrogen bond and thus the O–H stretch would be expected at lower frequency.[15a] It is well known that the (*Z*)-enol is considerably less stable to re-ketonization than is the (*E*)-form[5,17] and one may expect a very low barrier for this process. The evidence is consistent with the notion that (**5***Z*) may be formed from (**1**) in the nitrogen matrix, but may rapidly revert to starting material *via* a tunnel reaction. A similar conclusion has recently been drawn from the studies of the *o*-tolualdehyde system.[17c]

An assignment of the primary photoproduct to the enol (**5***E*) finds additional support in the photochemical behaviour of deuteriated (**1**). A collection of new bands (3 657w, 2 698m, 2 110s, 2 098s, 2 095(sh), 1 628w, 1 538w, 1 344m, 1 235w, 1 163w, 1 141m, 1 030m, 975w, and 726m,) was seen in the IR spectrum of the sample irradiated with at 313 nm. The analysis of the spectrum is difficult due to incomplete isotopic labelling, but important vibrations can be analysed. As was expected, the deuteriation slightly affected the ketene stretching vibrations (2 110, 2 098, and 2 095 cm^{-1}) and the CO stretch (1 141 cm^{-1}). A typical shift was seen for the stretching vibration of the OD group (2 698 cm^{-1}).

The enol can be photochemically generated from the (**1***EZ*) rotamer and it was not surprising that all absorptions due to starting material (Table 1) disappeared with differing rates. The yield of the photoenol was relatively high and the photochemically induced rotation of the formyl group leading to the (**1***EE*) $\longrightarrow$ (**1***EZ*) transformation was apparently much lower. The yield of photochemically induced rotation of the formyl group in many matrix-isolated substituted benzene derivatives was often found to be low.[15b,17c,18] As a result the absorptions due to the (**1***EE*) rotamer should decay much slower with the time of irradiation than those of (**1***EZ*). In fact, the bands labelled (with supercript *b*) in Table 1, representing a less reactive species, may be safely assigned to the (**1***EE*) rotamer.

All photochemical observations made for the argon-matrix-isolated (**1**) parallel those observed in nitrogen matrices. In these two matrices the primary photoproduct was stable when the matrices were heated up to a softening point, *i.e.* 35 K.

The UV–visible spectrum (Figure 2) assigned by us to (**5***E*) well correlates with the spectrum assigned by Scaiano and co-workers[5] to the cyclic enol (**4**). In our opinion, the transient absorption spectrum observed in the laser flash photolysis experiments might be due to a cyclic enol, but the low temperature spectrum in Scaiano's experiments, apparently very similar to the former, seems to be due to the enol (**5***E*).

Secondary Photochemical Reactions.—The primary photoproduct (**5***E*) is very sensitive to light and undergoes further photochemical transformations. The characteristic yellow colour of (**5***E*) is almost completely bleached when the sample is irradiated through a 357 nm cut-off glass filter for 40 min (Figure 2). Substantial changes could also be seen in the IR spectrum. The secondary photoproduct was characterized by a number of new bands, presented in Table 3. New bands observed in the carbonyl stretch region (1 790–1 755 cm^{-1}), characteristic of lactones, suggested the phthalide (**2**) as a candidate for the secondary photoproduct. Indeed, all observed

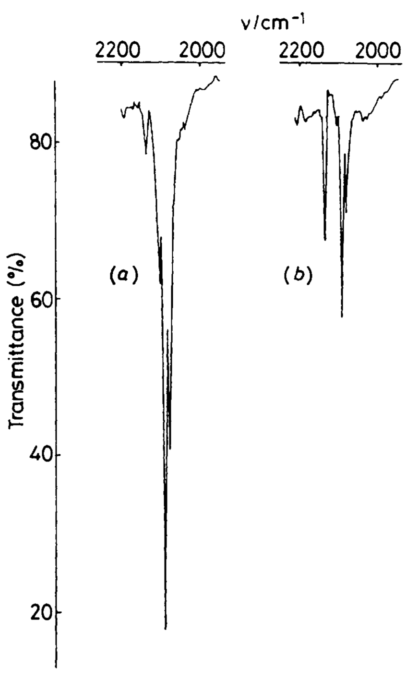
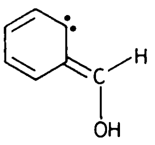


Figure 4. The carbon monoxide and ketene stretching region of the IR spectrum of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**) (*T* 15 K, *c* 6.6 mmol, *M*/*R* *ca.* 400). The sample was continuously irradiated through a 313 nm interference filter: (*a*) for 10 min; (*b*) for 70 min.

Table 4. Observed vibrational frequencies (cm^{-1}) assigned to the secondary photoproduct (λ 313 nm) of nitrogen-matrix-isolated *o*-phthalaldehyde (**1**).[a,b]

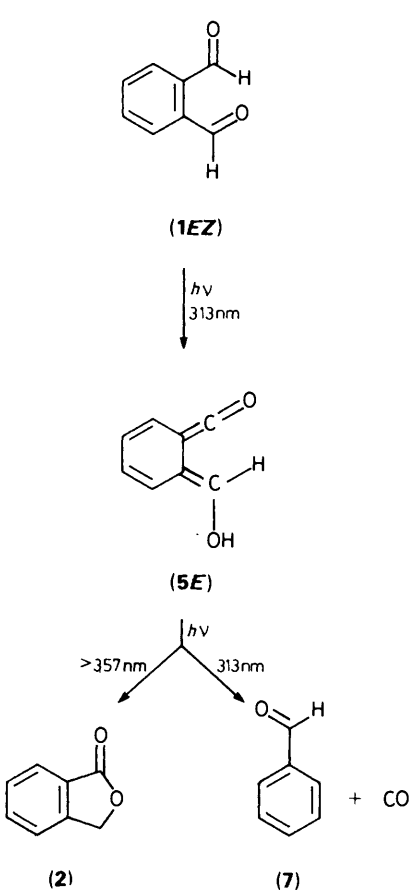
2 140m	1 312w	829m
1 712s	1 289w	749m
1 462w	1 202m[c]	692w
1 392w	1 168w	651w

[a] *T* 15 K, *c* 6.6 mmol, *M*/*R* *ca.* 400. [b] Observed vibrational frequencies of nitrogen-matrix-isolated benzaldehyde (**7**) given as a reference: 2 838w, 2 755w, 1 716s, 1 655w, 1 589m, 1 462m, 1 395w, 1 312m, 1 290w, 1 207s, 1 171m, 1 078w, 1 028w, 830s, 750s, 690m, 652m, and 615w. [c] Absorption superimposed on the band observed in starting material.



(**6**)

bands assigned to the secondary photoproduct had the same positions and relative intensities as the majority of the intense bands observed in the IR spectrum of matrix-isolated (**2**) (Table 3). Two strong bands observed at 1 791 and 1 042 cm^{-1} in nitrogen-matrix-isolated (**2**) have not been seen in the analysed photoproduct. These bands, sensitive to matrix annealing, may represent a minor contribution from an unstable conformer of (**2**) trapped from the gas phase.



Scheme.

The situation was somewhat different when the primary photoproduct was further irradiated with a light of λ 313 nm. Prolonged irradiation caused a partial bleaching of the matrix and the IR spectrum, besides the signal due to carbon monoxide (2 140 cm^{-1}) (Figure 4), included other bands of the unknown product (Table 4). Also a noticeable amount of phthalide (**2**) was evidenced in the IR spectrum as a side product. The unknown product, formed together with CO after photofragmentation of the enol (**5***E*) with a light of λ 313 nm, should represent a carbene (**6**) or other product derived from (**6**). A new band in the OH-stretch region should accompany a stabilization of carbene (**6**). Since this is not the case, another product may be formed; benzaldehyde (**7**) is among the possible candidates. Indeed, the intense bands in the IR spectrum of nitrogen-matrix-isolated (**7**) correlate well with the bands presented in Table 4. The observed phototransformation of (**5***E*) is not surprising as similar photoreactions are known for other ketene intermediates.[19]

Conclusions

Among the two rotamers (**1***EZ*) and (**1***EE*) evidenced in the matrix-isolated (**1**) only (**1***EZ*) photoenolizes, leading to the mixture of enols (**5***E*) and (**5***Z*) from which only (**5***E*) is stabilized. The enol (**5***E*), upon further irradiation, undergoes intramolecular cyclization (λ > 357 nm) to phthalide (**2**) or fragmentation (λ 313 nm) to carbon monoxide and benzaldehyde (**7**). The observed phototransformations of matrix-isolated (**1**) are summarized in the reaction Scheme.

Acknowledgements

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References

1 J. Kagan, *Tetrahedron Lett.*, 1966, 6097.
2 S. P. Pappas and J. E. Blackwell, Jr., *Tetrahedron Lett.*, 1968, 3337.

3 K. F. Cohen, J. T. Pinhey, and R. J. Smith, *Tetrahedron Lett.*, 1968, 4729.

4 D. A. Harrison, R. N. Schwartz, and J. Kagan, *J. Am. Chem. Soc.*, 1970, **92**, 5793.

5 J. C. Scaiano, M. V. Encinas, and M. V. George, *J. Chem. Soc., Perkin Trans. 2*, 1980, 724.

6 I. R. Dunkin, *Chem. Soc. Rev.*, 1980, **9**, 1.

7 R. N. Perutz, *Annu. Rep. Prog. Chem., Sect. C, Phys. Chem.*, 1985, **82**, 157.

8 R. S. Sheridan, *Org. Photochem.*, 1987, **8**, 159.

9 J. Gębicki and S. Kuberski, *J. Chem. Soc., Chem. Commun.*, 1988, 1364.

10 F. Weygand, K. Fogelbach, and K. Zimmerman, *Chem. Ber.*, 1947, **80**, 391.

11 H. Lumbroso, C. Liegeois, G. C. Pappalardo, and V. Librando, *J. Mol. Struct.*, 1980, **62**, 195.

12 D. Mirachi, L. Phillips, H. Lumbroso, and G. L. D. Ritchie, *Aust. J. Chem.*, 1984, **37**, 465.

13 T. Schafer, G. H. Penner, R. Sebastian, and C. S. Takeuchi, *Can. J. Chem.*, 1986, **64**, 158.

14 (*a*) C. E. Blom, R. P. Muller, and H. H. Gunthard, *Chem. Phys. Lett.*, 1980, **73**, 483; (*b*) J. Gębicki and A. Krantz, *J. Am. Chem. Soc.*, 1981, **103**, 4521; (*c*) J. Gębicki and S. Kuberski, unpublished work.

15 (*a*) M. D. Joesten and L. J. Schaad, 'Hydrogen Bonding,' Marcel Dekker, New York, 1974; (*b*) J. Gębicki and A. Krantz, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1617.

16 J. Gębicki, S. Kuberski, and J. Michalak, unpublished work.

17 (*a*) P. G. Sammes, *Tetrahedron*, 1976, **32**, 405; (*b*) R. Haag, J. Wirz, and P. J. Wagner, *Helv. Chim. Acta*, 1977, **60**, 2595; (*c*) J. Gębicki and A. Krantz, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1623.

18 J. Gębicki and S. Kuberski, unpublished work.

19 (*a*) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, 1973, **95**, 244; (*b*) O. L. Chapman, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *ibid.*, 1973, **95**, 4061; (*c*) O. L. Chapman, C.-C. Chang, J. Kolc, N. R. Rosenquist, and H. Tomioka, *ibid.*, 1975, **97**, 6586; (*d*) A. Krantz and B. Hoppe, *ibid.*, 1975, **97**, 6590.

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