# Thermochromism and Thermal *E,Z* Isomerizations in Bianthrones[1a]

Yitzhak Tapuhi,[*1b] Ofra Kalisky,[1c] and Israel Agranat[*1b]

Department of Organic Chemistry and Department of Physical Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel

The standard heat of the thermochromic equilibrium A ⇌ B in bianthrones (1) was investigated in the temperature range 40–220 °C, with special emphasis on steric effects. The data indicate that there is no direct correlation between $\Delta H°$ values and possible steric interactions in the vicinity of the central double bond. The thermal decay of the colored B species of 2,2'-bis(trifluoromethyl)bianthrone (3) was studied by laser flash photolysis. The relation between the thermochromic process and the fast thermal *E,Z* isomerization found in the bianthrone series is discussed. It is concluded that both thermal phenomena have a common transition state.

Thermochromism, the phenomenon of reversible change of color with change of temperature,[2] was first revealed in bianthrone (1) at the beginning of the century.[3] The thermochromism of bianthrones in solution was shown[4] to result from a thermal equilibrium between two distinct and interconvertible isomeric species A ⇌ B, where A is the ground-state species and B is the thermochromic green species absorbing at 650–730 nm.[2] A–B type species were detected also (along with other isomers) in the photochromic phenomenon exhibited by bianthrones. It is generally accepted that the thermochromic B species and the photochromic B species are identical,[2b,e,g,5,6]


1 , X = C=O
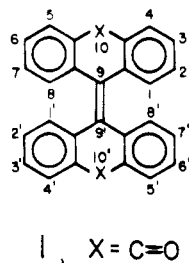
The structure of the thermochromic B species of bianthrone has puzzled theoreticians and experimentalists through the years, and many suggestions as to its molecular structure have been put forward.[2,7,8] Introduction of bulky substituents (bulkier than fluorine) at positions ortho to the central double bond ("pinch") deprived these bianthrones of their thermochromic characteristics, although they do remain photochromic.[2,9] It was recognized that the inhibition of thermochromism is associated with steric interactions in the vicinity of the "pinch" which prevent the molecule from passing to the thermochromic B species in the ground state by a thermal pathway.[2b-d] The thermal reversion B → A was studied by spectroscopic methods at low temperatures[10] and by flash methods at ambient temperature.[11,12] All reports claim a first-order behavior, with activation energies depending somewhat on the substituents and on the solvent and ranging from 13 to 16 kcal/mol. There were not any significant differences in this respect between bianthrones substituted at the 1 and 1' positions and other bianthrone derivatives. It is not exactly clear whether the flash studies (at ambient temperature) followed only the B → A reaction. This ambiguity stems from the possible appearance (in some cases) of photochromic C type isomers as intermediates, as well as other irreversible reaction products which absorb in the same region.[13]

The heat of the reaction A (Δ) ⇌ B ($\Delta H°$) could be obtained from the direct spectroscopic measurements in the visible region.[2a-d] The results indicated that the $\Delta H°$ values were dependent on the substitution pattern and on the type of substituents and ranged from 1.7 to 6.7 kcal/mol.

Among the various tentative structures proposed for the thermochromic B species of bianthrone, the *twisted conformation* (which had been suggested a score of years ago),[14,15] has gathered considerable experimental and theoretical support.[8] In this structure, the two anthrone halves of the molecule are twisted about the axis of the "pinch", while each of them preserves coplanarity. The transformation from the folded ground-state A species to the twisted B species (Figure 1) of bianthrone was claimed to be responsible for the observed thermochromism. The inhibition of thermochromism by bulky substituents at the 1 and 1' positions was explained[2a,b] assuming that the unfavorable steric interactions of the substituents with the bucking hydrogens at the opposite half of the molecule make the twisting into the B species impossible. The high value of $\Delta H°$ for the A (Δ) → B transformation obtained in the case of 2,2',4,4'-tetramethylbianthrone ($\Delta H° = 6.7$ kcal/mol) as compared with the parent compound ($\Delta H° = 3.2$ kcal/mol) was explained[2a,b] in terms of unfavorable steric interactions between the methyl groups in the 2 and 2' positions and the hydrogens in the 7' and 7 positions, creating difficulties in the twisting process. In principle, two geometrical isomers of the twisted B species are expected in appropriately substituted bianthrones, the *E* form and the *Z* form. The possible existence of *E,Z* isomerism in the B species of substituted bianthrones was overlooked in the studies of the thermochromism in this series.

DNMR studies of steric effects on the pathways for *E,Z* isomerization and conformational inversion in 2,2'-disubstituted bistricyclic ethylenes (including bianthrones) indicated that the highest energy transition state for these conformational processes is the folded–twisted structure (TS-1, Figure 2) and not the biradical $\pi/2$ twisted ethylene (TS-2, Figure 2).[1a,16] This transition state exhibits one primary [H(1)–H(8')] steric interaction and one secondary [R(2)–H(7')] steric interaction. The verification of this unconventional pathway in the bianthrone series[1a] prompted a search for a possible relationship between thermochromism and the thermal *E,Z* isomerization in these systems. Toward this goal, a systematic study of the effects of steric interactions on thermochromism in bianthrones was undertaken.
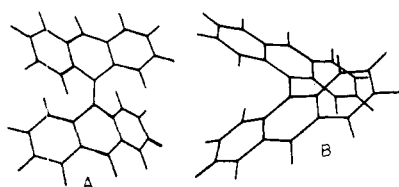

(*E*)-2, R = CH₃   (*Z*)-2, R = CH₃
(*E*)-3, R = CF₃   (*Z*)-3, R = CF₃
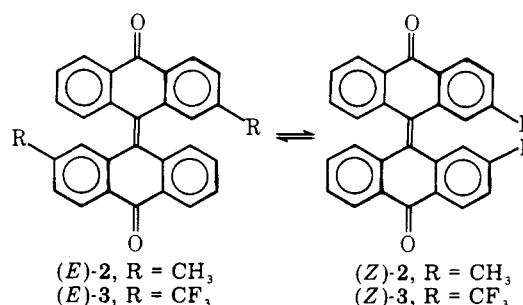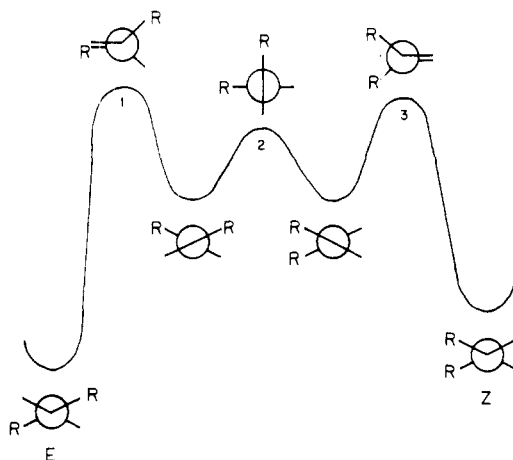
Figure 1. The folded A and the twisted B forms of bianthrone.

Figure 2. Proposed free-energy profile and isomerization pathway of *E,Z* isomerization in 2,2'-disubstituted bianthrones.
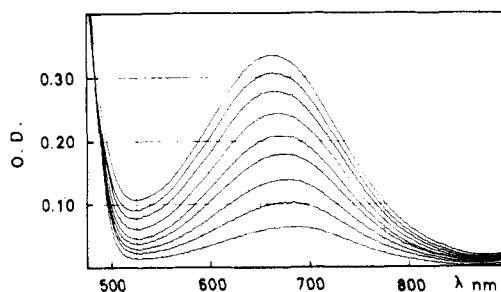

Figure 3. Optical absorbance of **2** at various temperatures in the region of the thermochromic band in dimethyl phthalate (see also Table II).
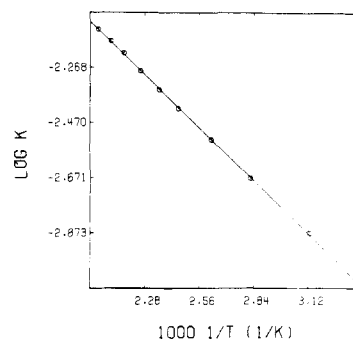

Figure 4. A plot of log *K* vs. 1/*T* for **2** in dimethyl phthalate.

Results and Discussion

The standard heat of the reaction A (Δ) $\rightleftharpoons$ B ($\Delta H°$) was studied by a method similar to the one previously used.[4] However, precautions were taken in order to obtain more reliable data. It should be noted that the $\Delta H°$(A (Δ) $\rightleftharpoons$ B) data reported in the literature often vary within a single derivative.[17] Thus, a systematic derivation of $\Delta H°$(A (Δ) $\rightleftharpoons$ B) data in one laboratory is advantageous. The following compounds have been studied: bianthrone (**1**), 2,2'-dimethylbianthrone (**2**), 2,2'-bis(trifluoromethyl)bianthrone (**3**), 2,2',3,3'-tetramethyl-6,6'-dibromobianthrone (**4**), 3,3'-dimethylbianthrone (**5**), 3,3'-dibromobianthrone (**6**), 3,3'-dimethoxybianthrone (**7**), and 2,2'-dimethyl-5,6:5',6'-dibenzobianthrone (**8**). Our measurements confirm that solutions of bianthrone and its derivatives obey Beer's law.[4]

Consider the equilibrium A (Δ) $\rightleftharpoons$ B at a given temperature *T* (K) and constant atmospheric pressure. Assuming ideal behavior, the equilibrium constant *K* at temperature *T* may be expressed as in eq 1, where C_B and C_A are molar concen-

$$K = C_B/C_A = \alpha/(1 - \alpha) \tag{1}$$

trations of B and A species, respectively, and α is the fraction of the compound in the B form. At a given temperature *T* we can obtain eq 2, where ϵ_T is the molar extinction coefficient

$$\alpha = \epsilon_T/\epsilon_B \tag{2}$$

at the thermochromic band maximum (in the region 650–730 nm) at temperature *T* and ϵ_B is the molar extinction coefficient at the same band maximum of the pure B species (implying that only the B species absorbs in this region). It is assumed that the ϵ values do not vary with temperature and that the change in ϵ_T stems only from the change of the relative population of B.

From eq 1 and 2 the equilibrium constants for the process A (Δ) $\rightleftharpoons$ B at each temperature were derived. ϵ_T values were obtained by a spectroscopic study of bianthrone solutions in the range of 40 to 220 °C (Figure 3). $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values were obtained from a plot of log *K* vs. 1/*T*, which gave a

straight line (Figure 4), relying on the well-known relation (at constant pressure) shown in eq 3.

$$d(\ln K)/dT = \Delta H°/RT^2 \tag{3}$$

The ϵ_B values needed for the evaluation of α values were previously[2a,4a] obtained by extrapolating a plot of ln ϵ_T vs. 1/*T* to *T* = ∞. The plot was found to be linear within the range of the measurements but is expected to be nonlinear at high *T* values. This method yielded inaccurate ϵ_B and α values. We have used ϵ_B values based on direct spectral measurements of pure B solutions obtained in the photochromic studies of bianthrone and its derivatives.[2e] ϵ_B values at the maximum of the thermochromic band were found to be equal to ϵ values of the lowest energy band (maximum at ~400 nm) of the A species and were practically independent of the substitution pattern.[2e] A value of 15 500 for ϵ_B was used throughout the present study.[2e] From the above-mentioned extrapolation, the value of 3548 for ϵ_B of bianthrone was obtained.[4a]

The $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values and the free energies of activation at coalescence temperature ($\Delta G^{\ddagger}_c$) for the process A_E (Δ) $\rightarrow$ A_Z (where available) are given in Table I.[1a] Table II summarizes the detailed results for **2**.

A careful analysis of the data in Table I seems to indicate that there is no direct correlation between $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values and the bulkiness of substituents at the 2 and 2' positions of bianthrone. It should be recalled that such a correlation does exist between $\Delta G^{\ddagger}_c$ values and the bulkiness of the 2 and 2' substituents[1] (Table I). This difference may be illustrated by comparing the data of compounds **2** and **4**. Whereas the $\Delta G^{\ddagger}_c$ values of both bianthrone derivatives are practically identical, reflecting the effect of the methyls at the 2 and 2' positions, the $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values differ markedly, presumably due to the effect of the other substituents. It seems that substitution at the 3 and 3' positions of **1** lowers the $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values. This trend (cf. $\Delta H°$ in **5, 6,** and **7**) is a consequence of electronic effects of the substituents rather than of steric effects.

Consider the proposed isomerization pathway (Figure 2) $A_E \rightleftharpoons A_Z$ for the bianthrone derivatives. The twisted B species

Table I. Heats of the Process A (Δ) $\rightleftharpoons$ B ($\Delta H°$) and Free Energies of Activation at Coalescence Temperature ($\Delta G^{\ddagger}_c$) for the Process A_E (Δ) $\rightarrow$ A_Z in Bianthrone Derivatives

compd	λ_{max}(48 °C), nm	$\Delta H°$(A (Δ) $\rightarrow$ B),[a] kcal/mol	$\Delta G^{\ddagger}_c$(A_E (Δ) $\rightarrow$ A_Z),[b] kcal/mol
bianthrone (1)	675	3.0 (3.4,[4a] 3.2,[4b] 3.5[10a])	
2,2'-dimethylbianthrone (2)	682	3.3	20.0
2,2'-bis(trifluoromethyl)bianthrone (3)	657	4.2	21.5
2,2',3,3'-tetramethyl-6,6'-dibromobianthrone (4)	709	1.9	20.3
3,3'-dimethylbianthrone (5)	698	2.4 (2.9[10a])	
3,3'-dibromobianthrone (6)	688	2.4 (4.1[10a])	
3,3'-dimethoxybianthrone (7)	724	1.3 (1.7[10a])	
2,2'-dimethyl-5,6:5',6'-dibenzobianthrone (8)	712	4.3	22.7

[a] In dimethyl phthalate as solvent; accuracy is ±0.2 kcal/mol. [b] Accuracy is ±0.3 kcal/mol; see ref 1a for experimental details.

Table II. Conversion Factors (α) and Equilibrium Constants (K) at Various Temperatures in Dimethyl Phthalate for 2

t, °C	$10^3\alpha$	10^3K
47.0	1.347	1.349
81.5	2.171	2.176
108.5	3.043	3.053
135.0	3.997	4.013
152.0	4.705	4.728
170.0	5.553	5.584
187.5	6.493	6.535
202.0	7.207	7.259
217.0	7.967	8.031

are assumed to be low concentration intermediates in this process. In principle, two B species are expected (in appropriately substituted bianthrones), B_E and B_Z. Therefore, the derived $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values represent an average heat of the reaction A_E + A_Z (Δ) $\rightleftharpoons$ B_E + B_Z because the two geometrical isomers of both species are undistinguishable in the electronic spectra.

It is reasonable to assume that the twisted B structures tend to prevent additional steric interactions between the 2, 2', 7, and 7' positions, at least when these positions are substituted by relatively small substituents, such as methyl. It is not known whether the higher $\Delta H°$ value of 3 represents the steric effect of the bulkier CF_3 groups or is a consequence of its electronic effect. The latter explanation is more likely as no direct correlation seems to exist between the bulkiness of 2 and 2' substituents and $\Delta H°$(A (Δ) $\rightleftharpoons$ B) values. The attempted explanation of inhibition of thermochromism (high $\Delta H°$ values) by steric interactions that interfere with the process of twisting is incorrect because it is related to the transition state of the process A (Δ) $\rightarrow$ B, while only relative steric interactions in the B and A species are expected to influence the thermochromic equilibrium.

The question of total disappearance of thermochromism by introduction of substituents (bulkier than fluorine) at the 1 and 1' positions of the bianthrone system may be withdrawn in view of the findings that only E isomers exist in these bianthrone derivatives.[1a] The corresponding Z isomers of these derivatives would convert rather easily to the B species by twisting via the unsubstituted side of the molecule (this path being open) and would therefore be thermochromic. Only the corresponding E isomers are blocked on both sides by the 1 and 1' substituents, which prevent the twisting by raising the energy of the transition state for the process.

Consider the transition state for the thermochromic process A (Δ) $\rightleftharpoons$ B. A plausible hypothesis is to identify this transition state with the folded–twisted transition state (TS-1 and TS-3) for the E,Z isomerization (Figure 2). This structure exhibits a single 1,1' primary steric interaction and is consistent with

the void of thermochromism in 1,1'-disubstituted bianthrones with bulky groups.

The hypothesis of a common transition state for both processes implies that the energy barrier of E,Z isomerization would be practically equal to the sum of the heat of the process A (Δ) $\rightleftharpoons$ B ($\Delta H°$) and the activation enthalpy for the thermal reversion B (Δ) $\rightarrow$ A [$\Delta H^{\ddagger}$(B (Δ) $\rightarrow$ A)]. It is assumed that the energies of TS-1 and TS-3 in the isomerization pathway are close, so that the B (Δ) $\rightarrow$ A transformations of both isomeric B forms have a very similar behavior and so that there is a facile equilibration between the B species through the lower energy TS-2. A combined process B_E + B_Z $\rightarrow$ A_E + A_Z is followed experimentally. The $\Delta S^{\ddagger}$ (entropy of activation) for the isomerization process A_E $\rightleftharpoons$ A_Z is expected to be very low.[1,16] On the basis of the assumptions given above, the equality shown in eq 4 may be postulated.

$$\Delta G^{\ddagger}_c(E \rightarrow Z) \approx \Delta H°(A\ (\Delta) \rightleftharpoons B) + \Delta H^{\ddagger}(B\ (\Delta) \rightarrow A)$$

$$(4)$$

In order to verify the validity of eq 4, ΔH(B (Δ) $\rightarrow$ A) in compound 3 was measured. As recalled, the colored B species in the thermochromic and the photochromic phenomena are identical. The B species (B_E + B_Z) of 3 were obtained (at ambient temperatures in sufficient concentrations) by the photochemical route using a laser flash photolysis system. In a recent flash study of bianthrone, it was shown that the photochromic C isomer is a precursor in the irreversible photochemical reactions of bianthrone in some polar solvents.[13] It seems that the B species are the major photoproducts even at ambient temperature in aromatic solvents.[12,18] In order to prevent possible disturbances in the measurement of the thermal decay of B by a C-type isomer or by irreversible reaction products (absorbing also in the region of the lowest energy absorption band of B), the measurements were conducted on compound 3. This derivative proved to be exceptionally stable to irreversible photoreactions, among the bianthrone derivatives not substituted in the 1 and 1' positions by methyls. The thermal decay of 3 was studied in toluene at three different wavelengths: 620, 650, and 680 nm (the B species of 3 obtained by heating a dimethyl phthalate solution had a peak at 657 nm at 48 °C). The highest absorbance values of the transient were obtained at 650 nm, and the three measurements were in good agreement. Hence, a practically pure B species of 3 was indeed followed. The decay (measured at four temperatures in the range of 25 to 50 °C) fitted first-order kinetics and was independent of concentration. At 25 °C a flash photoexcitation was used and the results fitted excellently with the laser results; diffusion could therefore be ruled out as contributing to the laser experiments (the contribution of diffusion was originally suspected because of the slow base time used for the measurements, 100–105 ms full-scale).

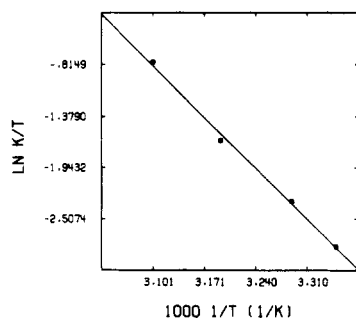The linear behavior of the decay and the absence of two

Figure 5. A plot of ln (K/T) vs. $1/T$ for the B $(\Delta) \rightarrow$ A decay of 3 in toluene (see Table III).

Table III. Kinetic Results of the Laser Flash Photolysis Experiments of B$(\Delta) \rightarrow$ A Decay of 3 in Toluene^a

t, °C	K,^{b} s^{-1}
29.5	17.8 ± 0.9
31.0	30 ± 1
40.2	61 ± 9
49.5	149 ± 8

^{a} Followed at 620, 650, and 680 nm. ^{b} Average values from three measurements at three different wavelengths.

different decay times point toward a similarity in the energies of the transition states TS-1 and TS-3 (Figure 2). The kinetic results are given in Table III. A linear dependence of ln (K/T) vs. $1/T$ (the correlation factor of the linear regression is 0.998) (Figure 5) yielded the $\Delta H^\ddagger$(B $(\Delta) \rightarrow$ A) value of 16.1 ± 0.7 kcal/mol. The ΔH°(A $(\Delta) \rightleftharpoons$ B) value of 3 is 4.2 ± 0.2 kcal/mol, so the sum ΔH°(A $(\Delta) \rightleftharpoons$ B) + $\Delta H^\ddagger$(B $(\Delta) \rightarrow$ A) in 3 equals 20.3 ± 0.9 kcal/mol. It is in fair agreement with the $\Delta G^\ddagger{}_c$($E \rightarrow Z$) value in 3 of 21.5 ± 0.3 kcal/mol.[1a] The latter value contains also an entropy term of ~0.8 kcal/mol (at the coalescence temperature 414 K) for the E,Z isomerization of 3 (assuming a low value of −2 eu for the entropy of activation). Hence, the enthalpy of activation for the E,Z isomerization process of 3 is estimated as ~20.7 kcal/mol. It may be concluded that the thermochromic phenomenon and the E,Z isomerization have a common transition state, the twisted-folded species. Our results are consistent with previous calculations which showed that the structure of the highest energy in the energy profile for torsion about the "pinch" in bianthrone is not the $\pi/2$ twisted biradical but a ~40° twisted species.[8]

Experimental Section

General. High temperature electronic absorption spectra of 1 and its derivatives were studied in dimethyl phthalate at concentrations in the range of 2×10^{-3} to 6×10^{-3} M. The change of the total concentration due to the expansion of the solvent was taken into account in the calculation of the concentration at each temperature, assuming that the dependency of the density ρ_t of the solvent on the temperature t (°C)[4a] is $\rho_t = 1.2070 - 0.00088t$. The absorbance at temperatures in the range of 40 to 220 °C was measured in a Beckman DK-2A double-beam spectrophotometer equipped with a copper block electrically heated to the desired temperature. The block was thermally insulated and equipped with a RFL Model 70 temperature controller. The stability of temperature was better than ±0.2 °C. Temperatures were measured inside the solution by means of a Chromel–Alumel thermocouple and are accurate within ±0.5 °C. At

least two different runs, each including nine readings in the above-mentioned temperature range, were taken for obtaining the ΔH°(A $(\Delta) \rightleftharpoons$ B) values. Each run gave a linear plot of log K vs. $1/T$ with a correlation constant of the linear regression higher than 0.997. The ΔH° values derived from data of different runs agreed within ±0.2 kcal/mol, and this is considered to be the accuracy of the ΔH° values given in Table I.

The N_2 pulsed laser flash photolysis system used in this study was previously described.[19] The exciting pulse has a 7-ns half-width at 337.1 nm. The monitoring beam was a pulsed Xe arc arranged in a collinear geometry with the exciting flash. The toluene solutions (1.01 × 10^{-4} M) were held in optical grade quartz cells of 1-cm optical path in a copper block, the temperature of which was controlled by means of a thermostat. The temperature stability was ±0.3 °C. Temperatures were measured by means of a Chromel–Alumel thermocouple inside the solution and are accurate within ±0.3 °C.

Materials. Compounds 5–7 were obtained from the late Professor E. D. Bergmann. Their synthesis and properties are described in ref 9a.

Registry No.—1, 434-85-5; (E)-2, 58821-85-5; (Z)-2, 58821-82-2; (E)-3, 58821-84-4; (Z)-3, 58821-83-3; (E)-4, 69611-32-1; (Z)-4, 69611-33-2; (E)-5, 69611-34-3; (Z)-5, 69611-35-4; (E)-6, 69611-36-5; (Z)-6, 69611-37-6; (E)-7, 69611-38-7; (Z)-7, 69611-39-8; (E)-8, 69611-40-1; (Z)-8, 69611-41-2.

References and Notes

(1) (a) The dynamic conformational behavior of bianthrones is described in the preceding paper: I. Agranat and Y. Tapuhi, *J. Org. Chem.*, companion paper, this issue. (b) Department of Organic Chemistry. (c) Department of Physical Chemistry.

(2) For reviews on the structure and the thermochromic, photochromic, and piezochromic properties in this series, see (a) G. Kortüm, *Angew. Chem.*, **70**, 14 (1958); (b) G. Kortüm, *Ber. Bunsenges. Phys. Chem.*, **78**, 391 (1974); (c) J. H. Day, *Chem. Rev.*, **63**, 65 (1963); (d) E. D. Bergmann, *Prog. Org. Chem.*, **3**, 81 (1955); (e) T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, **24**, 531 (1970); (f) G. H. Brown, Ed., "Techniques in Chemistry (New York)", Vol. 3, Wiley-Interscience, New York, 1971; (g) E. Fischer, *Fortschr. Chem. Forsch.*, **7**, 605 (1967).

(3) (a) H. Meyer, *Monatsh. Chem.*, **30**, 165 (1909); (b) *Ber.*, **42**, 143 (1909).

(4) (a) W. Theilacker, G. Kortüm, and G. Friedheim, *Chem. Ber.*, **83**, 508 (1950); (b) W. T. Grubb and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **72**, 419 (1950).

(5) I. D. Margerum and L. J. Miller, ref 2f, Chapter 6, p 557.

(6) G. Kortüm and G. Bayer, *Ber. Bunsenges. Phys. Chem.*, **67**, 24 (1963).

(7) J. F. D. Mills and S. C. Nyburg, *J. Chem. Soc.*, 308, 927 (1963).

(8) R. Korenstein, K. A. Muszkat, and S. Sharafy-Ozeri, *J. Am. Chem. Soc.*, **95**, 6177 (1973).

(9) (a) E. D. Bergmann and H. J. E. Loewenthal, *Bull. Soc. Chim. Fr.*, **19**, 66 (1952); (b) *J. Chem. Soc.*, 2572 (1953).

(10) (a) Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, 629 (1953); (b) T. Bercovici and E. Fischer, *Isr. J. Chem.*, **7**, 127 (1969).

(11) J. R. Huber, U. Wild, and Hs. H. Gunthard, *Helv. Chim. Acta*, **50**, 589, 841 (1967).

(12) L. J. Dombrowski, C. L. Groncki, R. L. Strong, and H. H. Richtol, *J. Phys. Chem.*, **73**, 3481 (1969).

(13) R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv. Chim. Acta*, **59**, 1826 (1976).

(14) G. Kortüm, W. Theilacker, H. Zeininger, and H. Elliehausen, *Chem. Ber.*, **86**, 294 (1953).

(15) E. Harnik, *J. Chem. Phys.*, **24**, 297 (1956).

(16) (a) I. Agranat and Y. Tapuhi, *Nouv. J. Chim.*, **1**, 361 (1977); (b) *J. Am. Chem. Soc.*, **100**, 5604 (1978); (c) *ibid.*, **101**, 665 (1979).

(17) W. Theilacker, G. Kortüm, H. Elliehausen, and H. Wilski, *Chem. Ber.*, **89**, 1578 (1956).

(18) H. H. Richtol, R. L. Strong, and L. J. Dombrowski, *Isr. J. Chem.*, **12**, 791 (1974).

(19) C. R. Goldschmidt, M. Ottolenghi, and G. Stein, *Isr. J. Chem.*, **8**, 29 (1970).