Enthalpies of Solvent Transfer of Reactants and Transition States in the Diels–Alder Reaction

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The cause of the solvent effect on the activation enthalpies of four Diels–Alder reactions has been examined. Calorimetric determinations of the relative enthalpies of the reactants in electron-donor solvents (dioxane, *o*-xylene) *vs.* more electronegative solvents (chloroform, chlorobenzene) reveals that, whereas electron-donor solvents stabilize the reactants, the more electronegative solvents stabilize the transition state. The solvent effect on the enthalpy of activation is a consequence of these two effects. The transition state in the Diels–Alder reaction behaves like an electron-rich system.

The enthalpy of transfer of a transition state from one solvent to another can provide valuable information concerning the geometry and electronic constitution of the transition state and thus give one a greater insight into the mechanism of a reaction.[1] In particular, if the transfer is from a solvent which is an electron donor to one which is an electron acceptor, then the transfer enthalpy should be a measure of the degree of electron deficiency (or the lack of it) of the transition state.

The Diels–Alder reaction is distinguished by having a mechanism which is believed to involve no production or loss of charges along the path from reactants to products.[2] Neutral reactants produce a neutral product in a single, usually symmetrical step. Although the dienophile in this reaction generally is a molecule having a considerable dipole, this dipole is incorporated unchanged into the product and there is no *a priori* reason to believe that it increases or decreases greatly along the reaction path. In harmony with the above is the observation that this reaction usually has little or no solvent effect on its rate or on its enthalpy of activation.[3]

One objection that can be raised against this picture of a thoroughly "nonpolar" reaction mechanism is the fact that many of the dienes and dienophiles which undergo the Diels–Alder reaction also form charge-transfer complexes with each other.[4] It is not clear whether these complexes are along the reaction path and whether the transition state in any way resembles a charge-transfer complex. The fact that changes in exo/endo adduct ratios have been observed as a function of solvent[5] suggests that there can be sufficient *differences* in the polarities of Diels–Alder transition states. The importance of ionic contributors to the resonance hybrid of the transition state has been invoked to explain differences in reactivity in the Diels–Alder reaction.[6] Recent studies of the pressure dependence of the rate of this reaction has led to the suggestion that the dipole moment of the transition state is much greater than that of the dienophile.[7] Finally, there are some examples of substantial solvent effects on the activation enthalpy of Diels–Alder reactions.[8]

Determination of the enthalpies of transfer of Diels–Alder transition states from one solvent to another may shed some light on some of the questions raised by the above facts.

Results and Discussion

Table I contains four Diels–Alder reactions which exhibit a solvent effect on their activation enthalpies.[9] (See Charts I and II). In Table II are listed the results

TABLE I

SOLVENT EFFECT ON THE ENTHALPIES OF ACTIVATION OF DIELS–ALDER REACTIONS

Reactants	Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\delta\Delta H^{\ddagger}$, kcal/mol
Anthracene and maleic anhydride	Dioxane	15.7[a]	−3.2
Anthracene and maleic anhydride	Chloroform	12.5[b]	
Dimethylanthracene and maleic anhydride	Dioxane	10.3[a]	−2.9
Dimethylanthracene and maleic anhydride	Chloroform	7.4[b]	
Anthracene and tetracyanoethylene	*o*-Xylene	12.3[c]	−4.8
Anthracene and tetracyanoethylene	Chlorobenzene	7.5[c]	
Norbornadiene and tetracyanoethylene	*o*-Xylene	17.5[c]	−4.0
Norbornadiene and tetracyanoethylene	Chlorobenzene	13.5[c]	

[a] J. Sauer, D. Lang, and A. Miedert, *Angew. Chem.*, **74**, 352 (1962). [b] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **77**, 6284 (1955). [c] Reference 8.

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(1) (a) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965); (b) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginsberg, and P. Steinhertz, *Chem. Commun.*, 194 (1968); (c) P. Haberfield, L. Clayman, and J. S. Cooper, *J. Amer. Chem. Soc.*, **91**, 787 (1969); (d) M. H. Abraham, R. J. Irving, and G. F. Johnston, *J. Chem. Soc. A*, 199 (1970); (e) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg, *J. Org. Chem.*, **36**, 1792 (1971); (f) P. Haberfield, J. Friedman, and M. F. Pinkston, *J. Amer. Chem. Soc.*, **94**, 71 (1972).

(2) (a) A. Wasserman, "Diels–Alder Reactions," Elsevier, Amsterdam, 1965; (b) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); (c) S. Seltzer in "Advances in Alicyclic Chemistry," H. Hart and J. G. Karabatsos, Ed., Academic Press, New York, N. Y., 1968, p 1; (d) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 7149 (1970).

(3) M. J. S. Dewar and R. S. Pyron, *J. Amer. Chem. Soc.*, **92**, 3098 (1970).

(4) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 177–178.

(5) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

(6) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 719; (b) ref 2a, pp 84–85.

(7) R. A. Grieger and C. A. Eckert, *Trans. Faraday Soc.*, **66**, 2579 (1970), calculated the dipole moments of the reactants, transition state, and product from their partial molal volumes and the pressure derivative of the dielectric constant factor of the solvent. For the reaction of maleic anhydride with isoprene this yielded dipole moments of 2.5 D for maleic anhydride (actual value = 3.95 D), 4.1 D for the transition state, and 4.0 D for the product (actual value = 4.46 D).

(8) P. Brown and R. C. Cookson, *Tetrahedron*, **21**, 1977 (1965).

(9) The reported uncertainty in the activation enthalpies of the four tetracyanoethylene reactions was ±0.5 kcal/mol or about one-tenth as large as the solvent effect. The same authors[8] also reported similar solvent trends in a more complete series of solvents, namely *o*-xylene, toluene, benzene, bromobenzene, and chlorobenzene ($\Delta H^{\ddagger}$ = 12.3, 11.0, 9.2, 7.5, and 7.4 kcal/mol, respectively, for the reaction with anthracene, and $\Delta H^{\ddagger}$ = 17.5, 16.0, 15.0, 13.5, and 13.8 kcal/mol, respectively, for the reaction with norbornadiene). There can therefore be little doubt that a solvent effect on $\Delta H^{\ddagger}$ is operative here and that the donor–acceptor quality of the solvent seems to be the principal variable.

TABLE II
HEATS OF SOLUTION

Solute	Registry no.	Solvent	Registry no.	ΔH_s, kcal/mol[a]
Anthracene	120-12-7	Dioxane	123-91-1	5.34
Anthracene		Chloroform	67-66-3	5.22
Dimethylanthracene	781-43-1	Dioxane		5.52
Dimethylanthracene		Chloroform		4.85
Maleic anhydride	108-31-6	Dioxane		2.52
Maleic anhydride		Chloroform		3.77
Anthracene		*o*-Xylene	95-47-6	5.68
Anthracene		Chlorobenzene	108-90-7	5.88
Norbornadiene	121-46-0	*o*-Xylene		0.00
Norbornadiene		Chlorobenzene		0.00
Tetracyanoethylene	670-54-2	*o*-Xylene		0.33
Tetracyanoethylene		Chlorobenzene		5.29

[a] Concentrations ranged from 0.01 to 0.1 *M*. No changes in molar heat of solution with concentration were observed in this range. The standard deviations for the ΔH_s values ranged from 0.04 to 0.23 kcal/mol.

CHART I

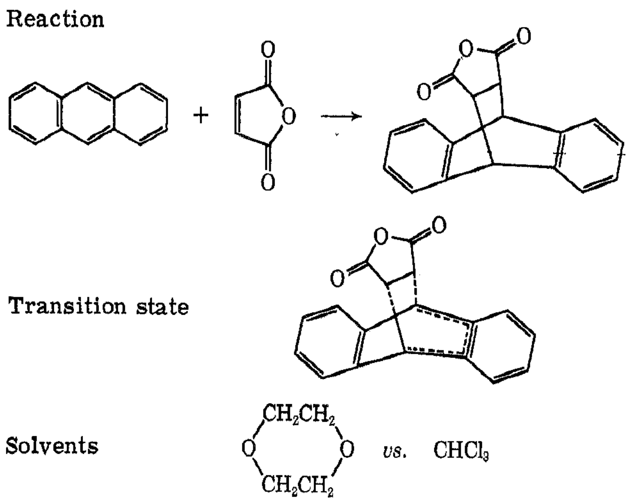
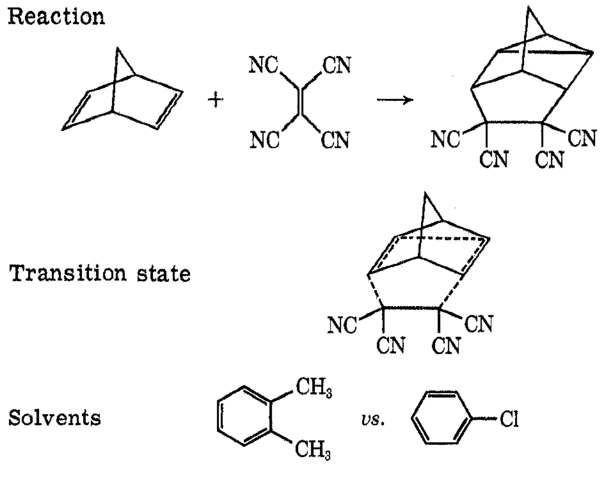


CHART II



of our calorimetric measurements of the heats of solution, ΔH_s, in the appropriate solvents, of the reactants in these four reactions. The enthalpy of transfer of a transition state, δH^t, is obtained from the relations $\delta H^t = \delta\Delta H_s^r + \delta\Delta H^{\ddagger}$, where $\delta\Delta H_s^r$ is the enthalpy of transfer of the reactants from one solvent to another, and $\delta\Delta H^{\ddagger}$ is the difference in the enthalpies of activation of the reaction in the two solvents. The enthalpies of transfer of the reactants, $\delta\Delta H_s^r$, and of the transition states, δH^t, for the above four Diels–Alder reactions are listed in Table III.

TABLE III
ENTHALPIES OF SOLVENT TRANSFER OF REACTANTS, $\delta\Delta H_s^r$, AND TRANSITION STATES, δH^t (KCAL/MOL)

Reaction	Solvent	$\delta\Delta H_s^r$	δH^t
Anthracene + maleic anhydride	Dioxane ⟶ Chloroform	1.1	−2.1
Dimethylanthracene + maleic anhydride	Dioxane ⟶ Chloroform	0.6	−2.3
Anthracene + tetracyanoethylene	*o*-Xylene ⟶ Chlorobenzene	5.2	0.4
Norbornadiene + tetracyanoethylene	*o*-Xylene ⟶ Chlorobenzene	5.0	1.0

As can be seen, the solvent effect on the activation enthalpies in the reaction of maleic anhydride with anthracene and with dimethylanthracene in dioxane and chloroform is caused by desolvation of the reactants (actually only the dienophile) and by superior solvation of the transition state in chloroform.[10] Since it is unreasonable to view the inferior solvation of maleic anhydride by $CHCl_3$ as being due to the greater polarity of $CHCl_3$, the principal solvent property determining the solvation enthalpy in this system must be the electron donating–releasing capacity of the solvent. Viewing the solvation enthalpy diagram (Chart III) of this reaction in this light we see that, while the reactant dienophile is an electron-deficient system (having an endothermic transfer enthalpy from dioxane to chloroform), the transition state behaves like an electron-rich system, having 2.1–2.3 kcal/mol more solvation energy in the more electronegative solvent, chloroform, than in the electron-donating solvent, dioxane.[11]

Turning to the second pair of reactions (Chart IV), that of tetracyanoethylene with anthracene and with norbornadiene, we see that the same general conclusions

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[10] It has been suggested by S. Seltzer (ref 2, p 17) that this solvent effect is not explicable in terms of a solvent–dienophile interaction only. Our results bear out this prediction.

[11] While it would not be surprising to find the transition state *less* electron deficient than the dienophile (because of electron delocalization in the transition state), it is remarkable that there is a *net effect* indicating that the transition state behaves as an electron donor toward the solvent. This property of the transition state cannot be mainly due to the diene because (1) the transfer enthalpy of the diene itself into the more electronegative solvent, though exothermic, is quite small, and (2) the exothermic transfer enthalpy of the dimethylanthracene transition state is only slightly greater than that of the anthracene transition state.

CHART III

RELATIVE ENTHALPIES (KCAL/MOL) OF REACTANTS AND TRANSITION STATES IN THE DIELS–ALDER REACTION OF MALEIC ANHYDRIDE WITH ANTHRACENE AND WITH DIMETHYLANTHRACENE IN DIOXANE AND IN CHLOROFORM

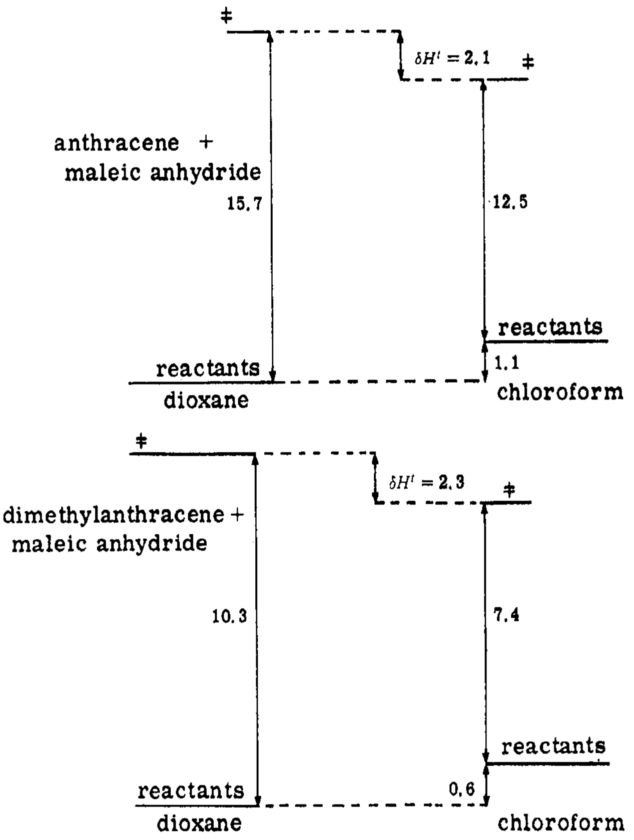
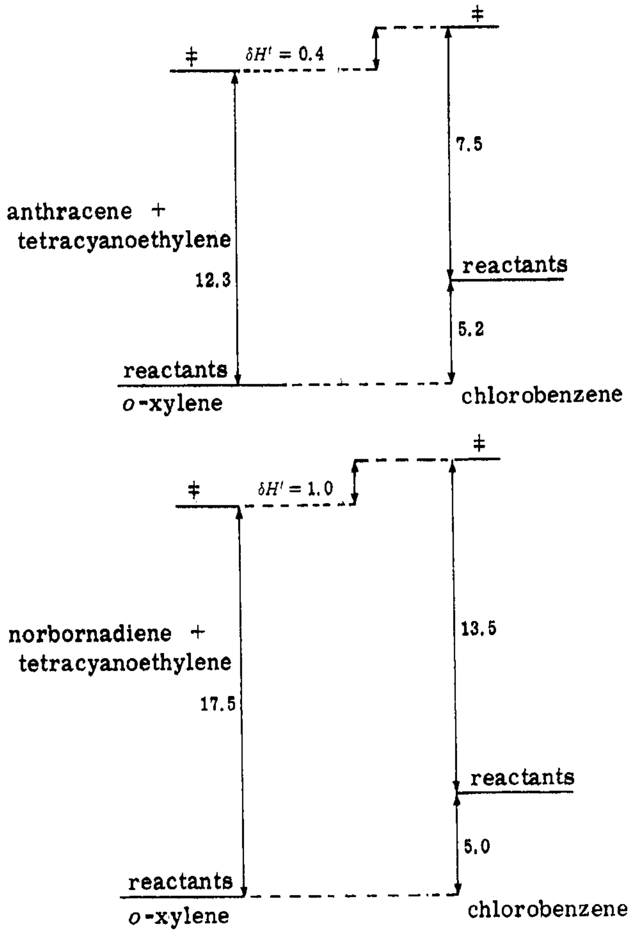


CHART IV

RELATIVE ENTHALPIES (KCAL/MOL) OF REACTANTS AND TRANSITION STATES IN THE DIELS–ALDER REACTION OF TETRACYANOETHYLENE WITH ANTHRACENE AND WITH NORBORNADIENE IN *o*-XYLENE AND IN CHLOROBENZENE



hold. Here the dienophile (tetracyanoethylene) is far more electron deficient than is the case for maleic anhydride and therefore its transfer enthalpy from an electron-donor solvent (*o*-xylene) to an electron-acceptor solvent (chlorobenzene) is even more highly endothermic (5.0 kcal/mol). Because of the extreme, intrinsic electron-withdrawing power of tetracyanoethylene, even the transition state containing the tetracyanoethylene moiety has an endothermic transfer enthalpy into the more electronegative solvent (0.4–1.0 kcal/mol). Thus in this case, because of the extreme nature of the dienophile, the net effect is that the Diels–Alder transition state behaves like an electron-poor system. However, here too the transition state behaves as a far more electron-rich entity than the diene plus the dienophile (by 4.0–4.8 kcal/mol).[12]

It therefore appears that solvent effects on the activation enthalpies of these Diels–Alder reactions are not to be understood in terms of solvent polarity (dielectric constant, dipole moment)[13] but rather in terms of the electron donor–acceptor property of the solvent and the different influence of this property on the reactants and on the transition state. (Some relevant solvent properties are shown in Table IV.) An electron-donor solvent lowers the energy of the dienophile while an electron-acceptor solvent lowers the energy of the transition state.

TABLE IV

SOLVENT PROPERTIES

	Dioxane	Chloroform	*o*-Xylene	Chlorobenzene
Dielectric constant	2.2^a	4.9^b	2.4^a	5.5^a
Dipole moment, Debye	0.3^c	1.1^c	0.5^c	1.5^c
E_T, kcal/mol	36.0^d	39.1^d		
Ionization potential, eV	9.5^e	11.4^e	8.6^e	9.1^e

[a] C. Marsden and S. Mann, "Solvents Guide," Interscience, New York, N. Y., 1963. [b] L. Scheflan and M. B. Jacobs, "Handbook of Solvents," Van Nostrand, New York, N. Y., 1953. [c] A. L. McClelan, "Tables of Experimental Dipole Moments", W. H. Freeman and Co., San Francisco, Calif., 1963. [d] C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 4, 29 (1965). [e] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Y. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martin's Press, New York, N. Y., 1966.

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(12) The suggestion that the Diels–Alder transition state, while structurally similar to products, is electronically similar to reactants (C. K. Ingold in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 119; see also R. A. Grieger and C. A. Eckert, ref 2d) is not supported by our observation of a large difference between the transfer enthalpy of the transition state and the transfer enthalpy of the reactants.

(13) The lack of correlation of the solvent effect with the dielectric constant has been pointed out by Dewar (ref 3) and others.

Experimental Section

Materials.—**Anthracene** (Aldrich) was recrystallized twice from benzene and then sublimed, mp 215.0–215.5°. **Maleic anhydride** (Fisher) was recrystallized twice from chloroform and sublimed, mp 53.0–53.5°. **Norbornadiene** (Eastman) was refluxed over $LiAlH_4$ and then fractionated, the fraction of bp 89–90° being used. **Tetracyanoethylene** (Aldrich) was recrystallized from dry chlorobenzene and sublimed, mp 198–199° (sealed tube). **9,10-Dimethylanthracene** was prepared according to the method of Phillips and Cason.[14] After two recrystallizations from benzene and sublimation it had mp 182–183°. **1,4-Dioxane** (Matheson Coleman and Bell, scintillation grade) was distilled from $LiAlH_4$, bp 101°. **Chloroform** (Matheson Coleman and Bell, Spectroquality) was dried over anhydrous $CaCl_2$ and distilled, bp 61°. **Chlorobenzene** (Aldrich) was passed through a column of Linde Molecular Sieves, 4A, and fractionated, the fraction boiling at 131° being used. ***o*-Xylene** (Eastman) was passed through a column of molecular sieves, 4A, and fractionated, the fraction distilling at 143° being used.

Heats of Solution.—The calorimeter and the procedure employed have been described previously.[1e]

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[14] D. D. Phillips and J. Cason, *J. Amer. Chem. Soc.*, **74**, 2934 (1952).

10-Ethoxy-9-phenanthroxyl Radical and Dimer

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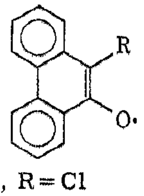
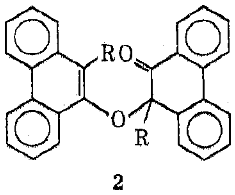
The dimer of the title radical **1b** is assigned a structure **3** different from that of the dimer **2** of the analogous chloro-substituted radical **1a**. The pmr spectrum of **3** is quite sensitive to temperature effects on the line widths and the epr spectrum of the radical **1b** is affected by solvent as well as by temperature. The spectra of **1a** and **2** are insensitive to solvent and temperature changes. The extent of dissociation of **3** has been measured in several solvents at several temperatures, and is found to increase with increasing solvent internal pressure. The chloro dimer **2** is more than an order of magnitude less dissociated than **3**. The rate constant for the disproportionation of **1b** to 10-ethoxy-9-phenanthrol, phenanthrenequinone, and ethylene is 19 M^{-1} sec^{-1} at 67°.

The dimers of 10-substituted 9-phenanthroxyl radicals, at one time believed to be peroxides, are now known to be keto ethers.[1] In the case of the 10-chloro dimer, the point of attachment of the ether linkage is at the 10 position, as shown in structure 2. This structure is supported by chemical evidence (only one of the two chlorine atoms is labile),[1,2] by the infrared spectrum,[1,2] and by the 90-MHz proton magnetic resonance spectrum,[2] which shows only aromatic protons.



1a, R = Cl
b, R = CH_3CH_2O

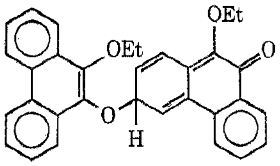


2

The properties of the 10-ethoxy-9-phenanthroxyl radical **1b** and its dimer were different enough from those of the chloro radical and dimer to warrant further investigation. Thus the ethoxy dimer is more dissociated and the line widths of its proton magnetic resonance spectrum are strongly temperature dependent, unlike those of the chloro dimer. Although the latter phenomenon proved not to be suitable for the measurement of dissociation rates[3] in this case, the equilibrium constant for the dissociation has been determined in a series of solvents by means of epr. The decomposition of **1b** into 10-ethoxy-9-phenanthrol, phenanthrenequinone, and ethylene was also studied.

Results and Discussion

Structure of the Ethoxy Dimer.—Although the infrared spectrum of the dimer of **1b** is that of a keto ether, the 90-MHz pmr spectrum has peaks in the vinyl region (doublet at δ 6.4, distorted triplet at δ 7.0), indicating a keto ether structure different from that of 2. On the basis of the position of the uv absorption maximum (340 nm in CCl_4, ε 4.10 × 10^3) **3** appears to be the most probable structure.[4]



3

The Temperature-Dependent Pmr Spectrum.—The 90-MHz proton magnetic resonance spectrum of the ethoxy dimer in $CDCl_3$ solution at 0, 25, and 40° is shown in Figure 1. The line broadening and narrowing effects shown in the figure are reversible, although samples heated for extended periods show peaks due to the decomposition product, 10-ethoxy-9-phenanthrol. The small triplet at δ 1.6 is assigned to the latter compound (Figure 1). Complete resolution of the spectrum for quantitative line width studies of the rate of dissociation is prevented by the presence of extra sets of peaks assigned to different conformers of the dimer.[5] These include three different and only partly resolved methyl group triplets centered at δ 0.6, 0.8, and 1.3, and overlapping quartets in the region of δ 2.8–3.7.

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[1] E. Müller, K. Schurr, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **627**, 132 (1954).

[2] R. E. Schwerzel, Dissertation, Florida State University, 1970.

[3] D. J. Williams and R. Kreilick, *J. Amer. Chem. Soc.*, **90**, 2775 (1968).

[4] Better evidence for **3** was sought by attempting to tautomerize the dimer to the totally aromatic ether by means of acidic and basic catalysts. Unfortunately, the prevailing reaction in all of these experiments was decomposition to phenanthrenequinone, for which polar as well as radical mechanisms can be envisioned.

[5] Molecular models indicate two possible isomeric folded structures for the dimer. Both structures are more compact than an extended structure and might be favored by the internal pressure of the solvent if not by π complexing between the ring systems of the two moieties. In one of the folded structures, each ethoxy group of one moiety is in the shielding region of an aromatic ring of the other moiety; the signal from these groups may be the large triplet at δ 0.6. In the other folded structure, the ethoxy groups are shielded less and to different extents, giving the triplets at δ 0.8 and 1.3.