

TABLE IV
VAPOR PRESSURE DATA FOR *trans-anti-trans*-
PERHYDROANTHRACENE

Point no.	<i>T</i> (°K.)	<i>P</i> (atm.)
1	274.5	1.16×10^{-6}
2	269.0	9.54×10^{-7}
3	282.8	4.82×10^{-6}
4	286.8	7.98×10^{-6}
5	289.2	9.43×10^{-6}
6	296.0	1.43×10^{-5}
7	299.8	2.18×10^{-5}
8	306.2	4.17×10^{-5}
9	312.6	8.61×10^{-5}

trans-syn-trans-perhydroanthracene is calculated to be 20.89 ± 0.57 kcal./mole. The heat of sublimation obtained for the *trans-anti-trans*-perhydroanthracene is 17.38 ± 0.79 kcal./mole. Hence, in the vapor phase the *trans-syn-trans* is energetically more stable than the *trans-anti-trans* isomer by 5.39 ± 0.86 kcal./mole.

Conclusion.—From the data reported above, the difference in energy of the chair and twist forms of cyclohexane is calculated to be approximately 4.79 ± 0.94 kcal./mole which is obtained simply by subtracting 0.6 kcal./mole from the experimentally observed difference in energy between hydrocarbons III and IV. The 0.6 kcal./mole value represents the sum of two 0.3 kcal./mole increments due to the two non-cancelling interactions of the terminal rings which exert a destabilizing effect on the twist form (see above). This new value for cyclohexane is in good agreement with the previous one of about 5.5 kcal./mole¹ and indicates that the estimation of the non-cancelling energy effect of the five-membered lactone ring was approximately correct.

Acknowledgments.—The authors wish to acknowledge the financial support of this work by the Wisconsin Alumni Research Foundation and the use of the computer facilities of the Numerical Analysis Laboratory of the University of Wisconsin.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Microwave Absorption and Molecular Structure in Liquids. L. The Dielectric Relaxation of Several Substituted Naphthalenes and 4-Acetyl-*o*-terphenyl^{1,2}

BY F. K. FONG³ AND C. P. SMYTH

RECEIVED AUGUST 20, 1962

The dielectric constants and losses at wave lengths of 1.25, 3.22, 10.0 cm. and 575 m. have been measured for 1-fluoronaphthalene, 1-acetonaphthone, 2-acetonaphthone and 4-acetyl-*o*-terphenyl in benzene solutions at temperatures from 20 to 60° and for 1-acetonaphthone at 25 and 50 cm. also. Refractive indices were determined for the sodium D-line at only one temperature. The data obtained for 2-acetonaphthone and 4-acetyl-*o*-terphenyl in benzene have been analyzed in terms of two relaxation times, the value of the relaxation time corresponding to the high frequency dispersion region being consistent with the intramolecular mechanism of acetyl group rotation. Rotation of the acetyl group in 1-acetonaphthone is prevented by steric hindrance, but large atomic polarization indicates liberation of the group. The heat of activation for rotational relaxation of the acetyl group is indistinguishable from the value of the resonance energy given by thermal data as the contribution of the group.

In dielectric investigations of substituted naphthalenes, it may be useful to have available the dielectric relaxation time of a molecule which shows a minimum difference in size and shape from the unsubstituted naphthalene molecule. For this reason, 1-fluoronaphthalene has been measured. The possibility of rotation of the strongly polar acetyl group in a molecule and the possible effects of steric hindrance and resonance energy are investigated in the present paper by determining the dielectric relaxation times of 1-acetonaphthone, 2-acetonaphthone, and 4-acetyl-*o*-terphenyl.

Experimental Methods

Apparatus.—The dielectric constants and losses of these molecules were measured in benzene solution by methods which have been previously described.⁴⁻⁶

Purification of Materials.—1-Fluoronaphthalene, 1-acetonaphthone, 2-acetonaphthone and 4-acetyl-*o*-terphenyl were obtained from the Eastman Kodak Company. 1-Fluoronaphthalene was fractionally distilled in a 91-cm. column utilizing a cold finger. The fraction collected had boiling points of 83.0°–83.2° (10 mm.), 80.8° (8 mm.), and 79° (7.5 mm.).

1-Acetonaphthone was fractionally distilled. The fractions collected had boiling points of 146.6° (50 mm.), 146.2° (4.5 mm.) and 146.0° (4.8 mm.).

2-Acetonaphthone was recrystallized from 60–70° benzene twice and was then vacuum dried in a desiccator containing anhydrous calcium chloride. The observed melting point was 55.8–56.1°. 4-Acetyl-*o*-terphenyl was used without further purification.

Benzene (Allied Chemical Corp.) was dried over "Drierite" (W. A. Hammond Drierite Company) for several weeks and then was used without further purification.

Experimental Results

Slopes a_0 , a' , a_D and a'' were obtained by plotting the static dielectric constants ϵ_0 , the high-frequency dielectric constants ϵ' , the refractive indices for the sodium D line, and the losses ϵ'' of the solutions against the concentrations of the polar solutes. Cole-Cole⁷ plots of a'' vs. a' were made in order to determine the distribution parameter α and the most probable relaxation time τ_0 .⁸

The experimental values for a_0 , a' and a'' obtained for these compounds are listed after each compound in Table I. The concentration range of the three solutions measured for each substance is given as mole fractions in parentheses. The values obtained for α , a_D , a_∞ and τ_0 , the "most probable relaxation time," are listed in Table II.

Discussion of Results

The relaxation time 12.6×10^{-12} sec. for 1-fluoronaphthalene at 20° in Table II and previously determined values in benzene solution, 15.8×10^{-12} for 1-chloronaphthalene⁹ and 18.0×10^{-12} for 1-bromo-

(1) This research was supported by Resources Research, Inc. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents part of the work submitted by F. K. Fong to the Graduate School of Princeton University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) Sayre Fellow, 1959–1960.

(4) H. L. Laquer and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4097 (1948).

(5) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(6) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(7) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, New York, N. Y., 1955, Chap. 11.

(9) H. Kramer, *Z. Naturforsch.*, **15A**, 66 (1960).

TABLE I
 SLOPES FOR THE DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON CONCENTRATION IN BENZENE SOLUTION

Wave length, cm.	20°		30°		40°		50°		60°	
	a'	a''	a'	a''	a'	a''	a'	a''	a'	a''
1-Fluoronaphthalene (0-0.047)										
1.25	1.60	0.92			1.70	0.88			1.62	0.82
3.22	2.45	1.11			2.53	0.90			2.41	0.71
10.0	3.23	0.496			2.95	0.34			2.69	0.245
575 m.	3.30				3.00				2.70	
1-Acetonaphthone (0-0.018)										
1.25	3.80	2.15			4.27	2.35			4.71	2.54
3.22	6.63	4.30			7.20	4.00			7.63	3.53
10.0	9.94	3.85			9.90	2.85			9.54	2.00
25	12.00	2.02			11.10	1.21			10.08	0.80
50	12.22	0.84			11.10	0.60			10.08	0.42
575 m.	12.40				11.30				10.10	
2-Acetonaphthone (0-0.0187)										
1.25	2.31	1.89	2.43	2.00	2.60	2.15	2.80	2.28	3.02	2.40
3.22	4.81	4.60	5.40	4.70	5.99	4.76	6.38	4.80	6.84	4.65
10.0	10.94	4.83	11.03	4.38	10.96	3.81	10.85	3.25	10.50	2.82
575 m.	14.25		13.60		13.00		12.38		11.79	
4-Acetyl- <i>o</i> -terphenyl (0-0.0186)										
1.25	2.15	1.15	2.30	1.25	2.38	1.27	2.47	1.47	2.52	1.60
3.22	2.68	2.53	2.80	2.70	2.89	2.82	3.11	3.00	3.22	3.10
10.0	5.30	4.60	5.73	4.70	6.25	4.84	6.80	4.70	7.61	4.63
575 m.	13.89		13.40		12.91		12.38		11.76	

TABLE II

SLOPES, a_D , FOR THE DEPENDENCE OF THE SQUARE OF THE REFRACTIVE INDEX ON CONCENTRATION, WITH INFINITE FREQUENCY INTERCEPTS a_∞ , RELAXATION TIMES τ_0 , AND DISTRIBUTION PARAMETERS α

Temp., °C.	a_D	a_∞	$\tau_0 \times 10^{12}$, sec.	α
1-Fluoronaphthalene (benzene)				
20	0.417	1.08	12.6	0
40		1.08	9.9	0
60		1.04	8.0	0
1-Acetonaphthone				
20	0.722	3.21	24.9	0.03
40		3.20	19.0	.02
60		3.16	14.1	.0
2-Acetonaphthone				
20	0.719	1.90	See Table III	0.07
30		1.90		.08
40		1.94		.09
50		1.98		.08
60		2.02		.05
4-Acetyl- <i>o</i> -terphenyl				
20	1.234	1.80	See Table III	0.09
30		1.80		.07
40		1.90		.07
50		2.02		.06
60		2.13		.03

naphthalene¹⁰ show the increase of relaxation time with size and polarizability of the halogen previously observed for the monohalogenated benzenes.¹¹

The relaxation time of the naphthalene molecule cannot be measured directly due to the absence of a permanent molecular dipole, but 1-fluoronaphthalene or quinoline can be used to obtain an estimate of the relaxation time of the naphthalene molecule, just as fluorobenzene and pyridine were used in an estimate for benzene.¹¹ It is seen from the Stuart-Briegleb atomic models that the 1-fluoronaphthalene and quinoline molecules depart but little from the size and shape of the naph-

thalene molecule, the former showing a slight protrusion at the fluorine atom and the latter showing a slight indentation at the nitrogen atom. No relaxation time is available for quinoline in benzene solution, but, for the much more viscous pure liquid,¹² the relaxation time is 44.0×10^{-12} at 20°, and, for the still more viscous solutions in Nujol,¹³ the value is 46.9×10^{-12} sec. at 20°.

As is evident from the Stuart-Briegleb model of 1-acetonaphthone, rotation of the acetyl group is blocked by the adjacent hydrogen atom on the 8-position, but libration of the group is possible. The dielectric results for this compound yield a Cole-Cole arc which deviates little from a Debye semi-circle. It appears, therefore, that 1-acetonaphthone relaxes essentially by one simple process. The 1-nitronaphthalene molecule is slightly smaller than the 1-acetonaphthone molecule. The relaxation time 22.8×10^{-12} sec. for 1-nitronaphthalene at 20° in benzene¹⁴ is correspondingly smaller than the value 24.9×10^{-12} sec. for 1-acetonaphthone in Table II, as it should be if the relaxation time of the latter is that of molecular rotation only.

A significant difference between the 1-acetonaphthone molecule and that of 2-acetonaphthone is the strong steric hindrance exerted on the acetyl group in the 1-position by the adjacent hydrogen atom on the 8-position. The 2-substituted acetyl group is virtually free of such hindrance to rotation. The large atomic polarization indicated for 1-acetonaphthone by the large difference 2.49 between its values of a_∞ and a_D probably arises from the libration of the acetyl group, while the value 12.35 for $a_0 - a_\infty$ for 2-acetonaphthone as compared to 9.19 for 1-acetonaphthone suggests group rotation. Analysis of the experimental data in Table I by the double-arc method¹⁵ yields values for τ_1 , the molecular relaxation time, τ_2 , the group relaxation time, and c_2 , the relative weight of the group relaxation process, which are listed in Table III.

(12) R. C. Miller and C. P. Smyth, *J. Am. Chem. Soc.*, **79**, 308 (1957).(13) E. N. DiCarlo and C. P. Smyth, *J. Phys. Chem.*, **66**, 1105 (1962).(14) R. W. Rampolla and C. P. Smyth, *J. Am. Chem. Soc.*, **80**, 1057 (1958).(15) F. K. Fong and C. P. Smyth, *J. Phys. Chem.*, **67**, 226 (1963).(10) F. Hufnagel, *Z. Naturforsch.*, **15A**, 723 (1960).(11) C. P. Smyth, *Proc. Natl. Acad. Sci. U. S. A.*, **42**, 234 (1956).

The 4-acetyl-*o*-terphenyl molecule is interesting in that the three phenyl rings in the molecule form a bulky residue in which little rotational motion of the rings is possible, while the acetyl group at one end is free from any steric hindrance to its rotation. The Cole-Cole arcs for this compound are similar to those for 2-acetonaphthone. For both compounds, the dispersion regions $a_0 - a_\infty$ are almost identical in magnitude. The distribution parameters α for these two compounds are also of the same order, those for 4-acetyl-*o*-terphenyl being slightly larger at lower temperatures and smaller at higher temperatures. For reasons similar to those in the case of 2-acetonaphthone, it appears that acetyl group rotation is also present in the 4-acetyl-*o*-terphenyl molecule. Analytical results by the double-arc method are listed in Table III.

TABLE III

RELAXATION TIMES BY THE DOUBLE-ARC METHOD FOR 2-ACETONAPHTHONE AND 4-ACETYL-*o*-TERPHENYL

	Temp., °C.	$\tau_1 \times 10^{12}$, sec.	$\tau_2 \times 10^{12}$, sec.	c_2
2-Acetonaphthone	20	33	7.3	0.14
	30	30	7.0	.14
	40	27	6.4	.14
	50	23	6.0	.15
	60	20	5.4	.15
4-Acetyl- <i>o</i> -terphenyl	20	100	7.5	.12
	30	88	6.8	.14
	40	78	6.2	.13
	50	65	5.7	.15
	60	53	5.0	.15

From Table III it is clear that both molecules relax predominantly by over-all molecular rotation. The closeness of the c_2 values for these two molecules is consistent with the similarity of the two dipole moments. The large relaxation time pertaining to the over-all molecular rotation τ_1 of 2-acetonaphthone has the value 33×10^{-12} sec. at 20° as compared to the value 24.9×10^{-12} sec. for that of 1-acetonaphthone. This is in agreement with the fact that 2-substituted naphthalenes usually have longer relaxation times than the corresponding substituted compounds because of greater volumes swept out in rotation. The volume swept out by the over-all molecular rotation of the 4-acetyl-*o*-terphenyl molecule is roughly three times that swept out by the 2-acetonaphthone molecule. It is, therefore, reasonable that the value of τ_1 for 4-acetyl-*o*-terphenyl, 100×10^{-12} sec. at 20°, should be three times that of 2-acetonaphthone. The small and almost identical relaxation times τ_2 are presumably due to the acetyl group rotation in both molecules. It should be pointed out, however, that such good agreement between the values for τ_2 for the two compounds as is exhibited in Table III is rather fortuitous, since the present approximate approach to systems with two relaxation processes cannot always be expected to give such agreement. An error of about 10% in the determination of τ_2 normally should be expected.

The acetone molecule in benzene solution has a relaxation time¹⁶⁻¹⁸ of 3.2×10^{-12} sec. at 20°. The volume swept out by an acetyl group rotation is larger than that by a free acetone molecular rotation around the axis perpendicular to the C=O bond. Also, an

(16) D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, **42A**, 114 (1946).

(17) F. J. Cripwell and G. B. B. M. Sutherland, *ibid.*, **42A**, 149 (1946).

(18) H. Vyas and H. N. Srivastava, *J. Sci. and Ind. Research*, **18B**, 399 (1959).

acetyl group rotation in either 2-acetonaphthone or 4-acetyl-*o*-terphenyl encounters a potential energy barrier caused by resonance. It seems reasonable, therefore, that τ_2 for an acetyl group rotation should have the value of 7.3×10^{-12} sec. at 20° in benzene.

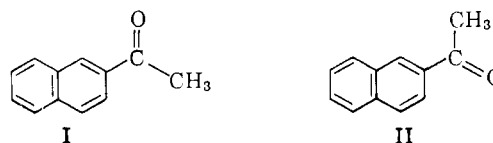
The free energies ΔF^* , heats ΔH^* and entropies ΔS^* of activation for dielectric relaxation, calculated in the usual manner,¹⁹ are given in Table IV. The second decimal place has no absolute significance but

TABLE IV

ACTIVATION ENERGIES (KCAL./MOLE) AND ENTROPIES (E.U./MOLE) IN BENZENE SOLUTION

	Temp., °C.	ΔF^*	ΔH^*	ΔS^*
1-Fluoronaphthalene	20	2.53	1.6	-3.3
	40	2.59	1.6	-3.3
	60	2.65	1.6	-3.3
1-Acetonaphthone	20	2.93	2.2	-2.44
	40	2.99	2.2	-2.45
	60	3.03	2.2	-2.43
2-Acetonaphthone (molecular rotation)	20	3.09	1.8	-4.5
	30	3.16	1.8	-4.6
	40	3.22	1.8	-4.6
	50	3.25	1.8	-4.6
	60	3.27	1.8	-4.5
4-Acetyl- <i>o</i> -terphenyl (molecular rotation)	20	3.74	2.5	-4.3
	30	3.82	2.5	-4.4
	40	3.88	2.5	-4.4
	50	3.90	2.5	-4.4
	60	3.91	2.5	-4.3
Acetyl group rotation	20	2.22	1.1	-3.8
	30	2.27	1.1	-3.8
	40	2.31	1.1	-3.8
	50	2.34	1.1	-3.8
	60	2.37	1.1	-3.8

is retained as possibly showing trends with temperature. Since the Stuart-Briegleb models show little steric hindrance of the acetyl group rotation in 2-acetonaphthone and 4-acetyl-*o*-terphenyl, resonance energy may make an important contribution to ΔH^* . In the case of 2-acetonaphthone, maximum resonance is achieved when the plane of the acetyl group is in the plane of the naphthalene nucleus. When the acetyl group is in such a position, it may be regarded as being in an equilibrium position. There are two such equilibrium positions which are equally probable



The two equilibrium positions are separated by an energy barrier the height of which is equal to the resonance energy contribution by the acetyl group to the molecule. The ΔH^* value, 1.1 kcal./mole, in Table IV for the acetyl group rotation is the activation energy barrier which the group encounters as it rotates. Within the large error in the analysis it is indistinguishable from the value for the resonance energy contribution of 1 kcal. to the acetophenone molecule²⁰ by the acetyl group determined calorimetrically.

(19) E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4102 (1948).

(20) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 99.