extraction of the residual aniline and decomposition of sulfite by addition of a small amount of hydrogen peroxide.

Procedure for Determination of the Dissociation Constant. The dissociation constants of the carboxylic acids and bisulfite were determined potentiometrically on systems comparable to those used in the study. For methylsuccinic acid pK_{a_1} and pK_{a_2} were determined to be 3.73 and 5.15, respectively; for succinic acid the previously reported values of 4.4 and 4.8 for pK_{a_1} and pK_{a_2} were used.[5] The dissociation constant for aniline was determined spectrophotometrically in a 0.05 *M* succinate buffer.

Hydrogen Bonding of Phenol to π Electrons of Aromatics, Polyolefins, Heteroaromatics, Fulvenes, and Azulenes[1]

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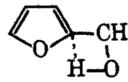
Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto, Japan. *Received March 29, 1966*

Abstract: Hydrogen-bond shifts and equilibrium constants of phenol–aromatic and phenol–olefin complexes in CCl_4 solution have been determined by the use of a grating infrared spectrophotometer. In a large excess of π base, the composition of the complexes has been confirmed to be 1:1. In the series of methyl-substituted benzenes as the proton acceptor, steric inhibition of complex formation by the methyl groups does not appear until durene. It is shown from the $-\Delta F$ *vs.* $\Delta\nu$ plot that complex stability increases as the π base is changed from monoolefins to conjugated diolefins, alkylbenzenes, and polycondensed aromatics. The meaning of the $-\Delta F$ *vs.* $\Delta\nu$ plot is discussed. From the comparison of the $-\Delta F$ *vs.* $\Delta\nu$ plots for furans and thiophenes with those for benzenoid hydrocarbons, it is concluded that the heteroaromatics act as π donors in the hydrogen-bonding interaction. The polar nonbenzenoid aromatic hydrocarbons, fulvenes, and azulenes have been found to be stronger proton acceptors than the less polar aromatic π bases. 4,6,8-Trialkylazulenes proved to be the strongest π bases ever studied. From the $-\Delta F$ *vs.* $\Delta\nu$ plots it is deduced that the importance of the 6π-electron cyclic conjugation structure is enhanced in fulvenes and azulenes in the hydrogen-bonded state.

Concerning the behavior of aromatics and olefins as the proton acceptor in hydrogen bonding,[2,3] serious discrepancies have appeared in the literature. Krueger and Mettee[4] reported that the association constants between methanol and methylbenzenes in CCl_4, as determined by the infrared spectroscopic method, go through a minimum value for *m*-xylene with the highest value for benzene. On this basis, they suggested the importance of steric hindrance of the methyl groups when the methanol molecule approaches the benzene ring. On the other hand, Basila, Saier, and Cousins[5] have stated that with an excess of benzene, ethylbenzene, or mesitylene in CCl_4 solution, *t*-butyl alcohol forms 1:2 as well as 1:1 complexes. Both these results differ from our findings. We found a linear relationship between log *K* and $\Delta\nu_{OH}$ for phenol–methylbenzene complexes on the assumption that all complexes are 1:1.[2] The first purpose of this paper is to discuss these discrepancies by a careful redetermination of $\Delta\nu_{OH}$ and *K* for phenol–π-base complexes.

This paper includes the results of the $\Delta\nu_{OH}$ and *K* determinations for various phenol–π-base complexes with azulene, fulvene, furan, thiophene, and their derivatives acting as proton acceptors. From their high reactivity in electrophilic substitution reactions,[6,7] the first two nonbenzenoid aromatics are expected to be very strong acceptors. Furan and thiophene are of particular interest, since there is some confusion in the literature on the donor character of these heteroaromatic hydrocarbons. Several authors favor a single donor ability, either π[8] or n,[9,10] while Pajak[11] proposes



a bifunctional donor character of furan from nmr measurements.

Experimental Section

Materials. Most of the chemicals were commercially available and were purified by the usual methods. Pyrene was purified according to the procedure of Clar.[12] Isopropylcyclopentadiene,[13]

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[1] (a) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 7, 1965. (b) Part IV, "Intermolecular Hydrogen Bond Involving a π Base as the Proton Acceptor."

[2] For pertinent literature see references cited in a previous paper of this series: part II, Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **87**, 1467 (1965).

[3] (a) R. J. Abraham, *Mol. Phys.*, 4, 367 (1961); (b) D. L. Powell and R. West, *Spectrochim. Acta*, 20, 983 (1964); (c) H. Dunken and H. Fritzsche, *Z. Chem.*, 2, 345 (1962); (d) B. Ghosh and S. Basu, *Trans. Faraday Soc.*, 61, 2097 (1965).

[4] P. J. Krueger and H. D. Mettee, *Can. J. Chem.*, 42, 288 (1964).

[5] M. R. Basila, E. L. Saier, and L. R. Cousins, *J. Am. Chem. Soc.*, 87, 1665 (1965).

[6] W. Keller-Schierlein and E. Heilbronner in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y. 1959, p 277.

[7] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, *Angew. Chem.*, **75**, 35 (1963).

[8] I. P. Gol'dshtein, E. N. Gur'yanova, and K A. Kocheshkov, *Z. Obshch. Khim.*, 32, 317 (1962); *Chem. Abstr.*, 57, 15933*c* (1962).

[9] T. Gramstad, *Spectrochim. Acta*, 19, 497 (1963).

[10] From infrared data, V. N. Novikov (*Materialy 4-oi* [*Chetvertoi*] *Nauchn. Konf. Aspirantov* (*Rostov-on-Don-Rostovsky. Univ.*) *Sb.*, 112 (1962); *Chem. Abstr.*, 60, 10518*a* (1964)) claimed that the hybrid orbital of oxygen in furan is trigonal and that in furfuryl alcohol the unshared electrons in this orbital form an intramolecular hydrogen bond with the OH group. This hydrogen bonding, however, could be due to an intramolecular O–H···π interaction as seen in benzyl alcohol (*cf.* M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, 32, 950 (1959)).

[11] (a) Z. Pajak and F. Pellan, *Compt. Rend.*, 251, 79 (1960); (b) Z. Pajak, *Arch. Sci.* (Geneva), 13, 527 (1960); *Chem. Abstr.*, 57, 16521*i* (1962).

[12] E. Clar, *Ber.*, **69**, 1683 (1936).

[13] K. Hafner, *Ann.*, **606**, 79 (1957).

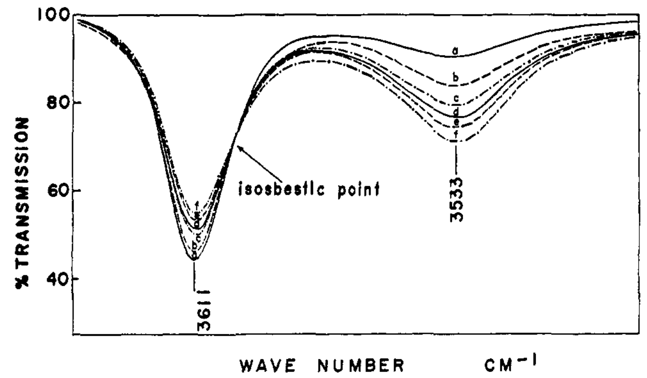

Figure 1. OH stretching absorption spectrum of 0.0121 *M* phenol in the presence of mesitylene in CCl_4. Initial concentrations (*M*) of mesitylene: (a) 0.292, (b) 0.596, (c) 0.700, (d) 0.838, (e) 0.988, (f) 1.145 (cell thickness 2 mm).

2,5-dimethylthiophene,[14] 2-methylthiophene,[15] azulene,[13] and 4,6,8-trimethyl- and 4,8-dimethyl-6-*t*-butylazulenes[16] were prepared by the known methods. Unfractionable impurities in 2-methylfuran, 2,5-dimethylfuran, and 2-methylthiophene were removed by preparative vapor phase chromatography. 6,6-Dialkyl- and 6-arylfulvenes were prepared by condensation of cyclopentadiene with carbonyl compounds in the presence of sodium ethoxide.[13] 6-(α-Furyl)fulvene was prepared according to the procedure of Schmidt.[17] Details of the synthesis and the spectral characteristics of the fulvenes discussed in this paper are described elsewhere.[18]

Measurements of Spectra. Hydroxyl stretching spectra of phenol in solutions of π bases in CCl_4 were recorded on a double pass grating infrared spectrophotometer Model DS-402G of Japan Spectroscopic Co., equipped with an Echellete having 180 lines/cm and blazed for first order at 2222 cm^{-1}. Wavenumbers were frequently calibrated.[19] Mechanical slit widths were kept constant at 250 μ, and the spectral slit width was 1.7 cm^{-1} in the region 3600–3400 cm^{-1}. The scanning speed was also kept constant at 20 cm^{-1} per 35–40 sec. Matched 2.00-mm cells with NaCl windows were used for double-beam operations. The procedure of obtaining ν_{OH} spectra of phenol in the presence of π base in CCl_4 has been described previously.[2a] Cells filled with solutions were irradiated by infrared light source for 15 min in the sample room of the spectrophotometer before scanning, until the cell temperature (measured by a thermistor inserted into the cell) reached the equilibrium temperature of 29.0 ± 0.1°. Scanning was repeated at least twice for each sample. In preparing each sample solution, the π base was freshly weighed in order to minimize error due to the concentration which is the most important in the spectrometric determination of equilibrium constants in the liquid phase.[3b]

The frequency of the bonded OH stretching absorption in "inert solvent" depends on the concentration of the proton-accepting base.[20] Fortunately, however, the *G* values[19,20] of aromatic hydrocarbons (benzene 80, toluene 74, mesitylene 72) are close to *G* for CCl_4 (69), so that no appreciable shifts of the bonded OH frequency due to the change of concentration of the aromatic proton acceptor was observed. The concentration of phenol was about 10^{-2} mole/l.

Analysis of Spectra. The previously[2] used mathematical resolution of the doublet spectra based on the Lorentz equation is not necessarily advantageous for two reasons: (1) two rewritings of the spectra required for the mathematical resolution (frequency calibration and conversion from transmission to optical density) make the spectra curve uncertain, and (2) the rewritings and calculations are very time consuming. Therefore, the free phenol concentration was estimated from the apparent peak absorbance of the free OH peak *minus* the absorbance at 3611 − $2\Delta\nu_{OH}$ cm^{-1}. The absorbance due to the free OH peak is virtually zero at this point.

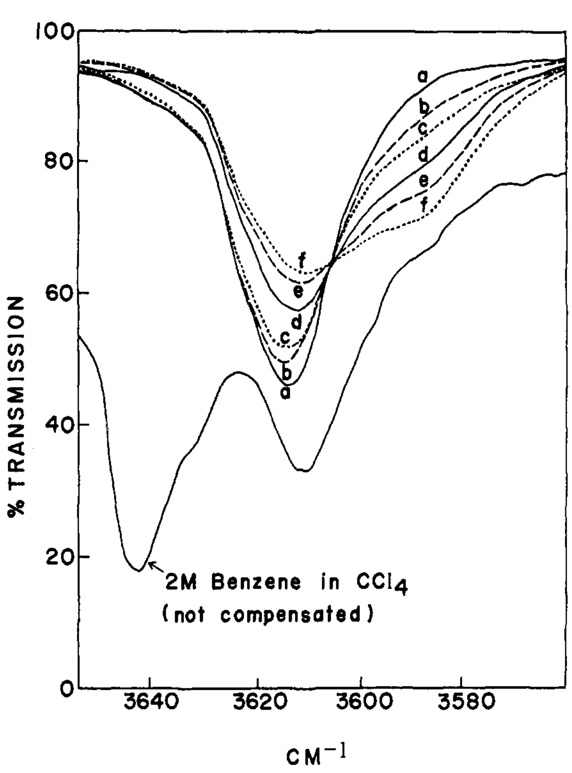

Figure 2. OH stretching absorption spectrum of 0.016 *M* *t*-butyl alcohol in the presence of benzene in CCl_4. Initial concentrations (*M*) of benzene: (a) 0, (b) 0.406, (c) 0.607, (d) 1.01, (e) 1.50, (f) 2.00 (cell thickness 5 mm).

The equilibrium constant *K* was calculated according to the equation[3b]

$$K = \frac{(\text{phenol})_0 - (\text{phenol})_f}{(\text{phenol})_f[(\text{base})_0 - (\text{phenol})_0 + (\text{phenol})_f]}$$

where suffixes 0 and f mean the initial and free concentrations, respectively. Independent measurements were repeated *ten times* for different concentrations of the proton acceptor. The two extreme *K* values obtained from the ten spectra were omitted. The *K*'s listed in Tables I to IV correspond to the average of eight data.

The apparent integrated molar absorption coefficient A^b of the bonded OH absorption was calculated as follows. The transmission was converted to the optical density, involving frequency calibration; the whole area under the spectra curve was measured by planimeter in the range $\nu^b_{max} \pm 2\Delta\nu^b{}_{1/2}$, where ν^b_{max} is the frequency of maximum absorption of the bonded OH peak and $\Delta\nu^b{}_{1/2}$ the half-width. The part of the area due to the free OH peak was subtracted from the whole area. From this difference, the intensity A^b of the bonded OH peak was obtained. The calculation included a correction (18.5%) for infinite integration.[21]

Results

The OH stretching vibrational spectra of phenol in the presence of aromatics, heteroaromatics, and alkylfulvenes were all simple doublets. The presence of isosbestic points with phenol-mesitylene (Figure 1) and *t*-butyl alcohol-benzene (Figure 2) systems excluded the possiblity of 1:2 complex formation, suggested by Basila and his co-workers.[5] This last system was examined under exactly the conditions of Basila, except that the cell thickness was reduced from 15 to 5 mm. The absorption spectra of 2 *M* benzene solution in CCl_4 at 5 mm thickness, illustrated in Figure 2, showed that Basila's cells were too thick, so that some of their spectra were probably insignificant. Furthermore,

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(14) G. N. Jean and F. F. Nord, *J. Org. Chem.*, 20, 1363 (1955).

(15) J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Am. Chem. Soc.*, 70, 3664 (1948).

(16) K. Hafner and H. Kaiser, *Ann.*, **618**, 140 (1958).

(17) H. Schmidt, *Ber.*, **90**, 1352 (1957).

(18) Z. Yoshida and E. Ōsawa, to be published.

(19) Z. Yoshida and E. Ōsawa, to be published.

(20) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).

(21) D. A. Ramsay, *ibid.*, 74, 72 (1952).

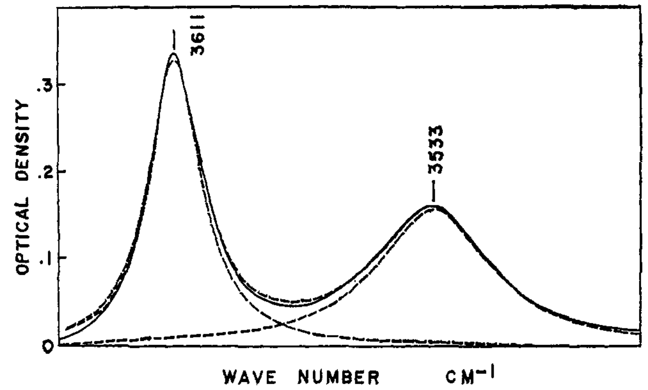

Figure 3. OH stretching absorption spectrum of 0.0149 *M* phenol in the presence of 1.10 *M* mesitylene in CCl_4. Dotted lines are analyzed component curves and synthesized curve.

a mathematical analysis based on the Lorentz function[2,21] of the OH stretching spectra of several phenol-mesitylene complexes (see Figure 3) indicated the presence of only one bonded species, since the sum of the two component curves was almost identical with the one observed.[22] Accordingly, the apparent doublet spectra were analyzed in terms of 1:1 complex formation only.

Tables I and II summarize the shifts and equilibrium constants obtained with aromatics, olefins, and heteroaromatics as π bases. The large uncertainty (*ca.* 10%) in the intensity determination is believed to be due to inherent machine deficiencies.[23]

When arylfulvenes and azulenes were used as proton acceptors, the ν_{OH} spectra split into a close triplet or a doublet with the bonded ν_{OH} peak unusually flat-topped, as shown in Figure 4. On the basis of the Lorentz equation, the ν_{OH} spectra could be resolved into three components reproduced in Figure 4 as broken lines. The splitting of the bonded OH band could be due either to (1) the double minimum potential function of the bonded OH stretching vibration or (2) the bifunctional donor properties of arylfulvenes and azulenes. The first explanation seems improbable since such a splitting has never been observed with other π bases including alkylfulvenes.[24] There is no reason to reject the second one. Therefore, the triplet was interpreted in terms of two basic centers α and β in the molecule (arylfulvenes and azulenes) with stretching vibrations OH···α and OH···β absorbing at different frequencies. Owing to the small initial mole ratio $[P_0/B_0 < 10^{-2}]$, both complexes will be of 1:1 composition.

$$\mathrm{PhOH} + \alpha \overset{K_\alpha}{\rightleftharpoons} \mathrm{PhOH}\cdot\alpha \qquad (1)$$

$$\mathrm{PhOH} + \beta \overset{K_\beta}{\rightleftharpoons} \mathrm{PhOH}\cdot\beta \qquad (2)$$

By assuming that the molar absorbances of the α and β bands were equal,[25] *K* could be calculated according to the following equations

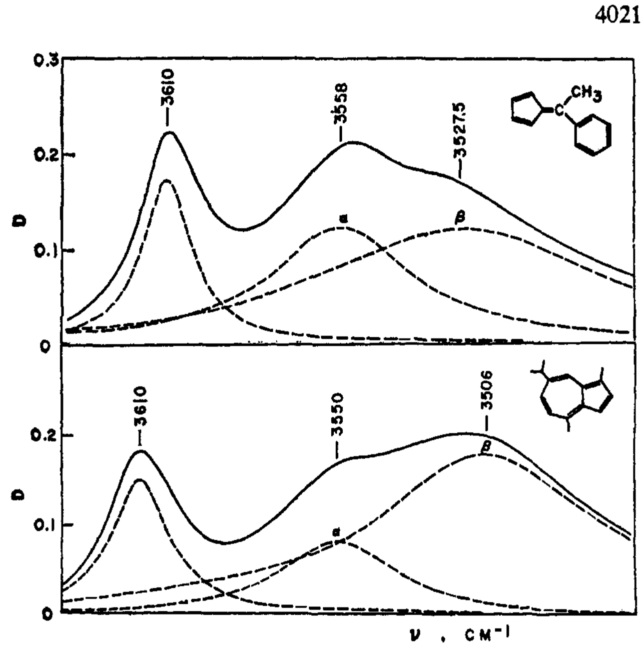

Figure 4. Triplet OH stretching absorption spectra of phenol in solutions of 6-methyl-6-phenylfulvene (1.84 *M*) and guaiazulene (2.00 *M*) in carbon tetrachloride: initial concentrations of phenol, 0.0162 and 0.0150 *M* (cell thickness, 2 mm); full line, observed; broken line, resolved.

$$K_\alpha = P_b/[1 + (A_\beta/A_\alpha)](1/P_fB_f)$$

$$K_\beta = P_b/[1 + (A_\alpha/A_\beta)](1/P_fB_f)$$

where $P_b = P_0 - P_f$, $B_f = B_0 - B_b = B_0 - P_b$, P_f and P_b are the concentrations of free and bonded phenol, B_f is the concentration of free π base, and A_α and A_β are the integrated α and β bands.

Table III summarizes the results with fulvenes and azulenes as proton acceptors. The data with 6-methyl-6-(1′-isobutenyl)fulvene (54) are inaccurate since the free OH band and the bonded OH band at about 3507 cm⁻¹ overlapped with the extremely broad third band. The last band was difficult to characterize and may be assigned to the OH bonded with the π system of the isobutenyl group. In contrast to other arylfulvenes, the absorption band of the OH bonded with 6-methyl-6-(*m*-nitrophenyl)fulvene (60) was a symmetrical singlet. From the close similarity of the spectral patterns, the large base-concentration dependence of ν_{OH} (bonded), and the equilibrium constants between 60 and 68 for nitrobenzene,[26] the hydrogen-bonding interaction takes place with the nitro group only.

Discussion

Phenol-Aromatic and Phenol-Olefin Complexes. Figure 5 shows an almost linear increase of $-\Delta F$ ($= RT \ln K$) of phenol-alkylbenzene complexes (open circles) with $\Delta\nu$, with the exception of the phenol-hexamethylbenzene complex. This $-\Delta F$ value is unusually low

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(22) In addition, the evidence for the bifurcated hydrogen bond reported in the literature has been open to question: *cf.* L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1963, p 135.

(23) E. D. Schmid, F. Langenbucher, and H. W. Wilson, *Spectrochim. Acta*, **19**, 835 (1963).

(24) In general a splitting of the hydrogen-bonded XH vibration spectrum in the fundamental stretching region due to double minimum potential has rarely been reported. For novel examples, see C. L. Bell and G. M. Barrow, *J. Chem. Phys.*, **31**, 1158 (1959); Y. Sato and S. Nagakura, *Nippon Kagaku Zasshi*, **76**, 1007 (1955).

(25) This assumption is rough. It would be more reasonable to estimate the molar absorbance for the α and β bands from $\Delta\nu_\alpha$ and $\Delta\nu_\beta$ values if the A^b *vs.* $\Delta\nu$ relationships presented by C. M. Huggins and G. C. Pimentel (*J. Phys. Chem.*, **60**, 1615 (1956)) and E. D. Becker (*Spectrochim. Acta*, **17**, 436 (1961)) are to be extended to small A^b and $\Delta\nu$ values. We did not extrapolate the Huggins-Pimentel line since our own A^b values shown in Tables I and III were widely scattered and the correlation between A^b and $\Delta\nu$ was poor.

(26) *Cf.* W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, **20**, 1635 (1964).

Table I. Frequency Shifts $\Delta\nu_{OH}$ of Phenol Due to Hydrogen Bonding with Aromatics and Olefins, Equilibrium Constants K of Hydrogen Bonding, and Spectral Properties of Bonded OH Stretching Bands in Carbon Tetrachloride

					Bonded OH[j]	
No.	π Base	Initial concn, M	$\Delta\nu_{OH}$, cm^{-1}	K (29°), l./mole	$A^b \times 10^{-3}$, l. mole^{-1} cm^{-2}	$\Delta\nu^b{}_{1/2}$, cm^{-1}
1	Benzene	0.53–1.4	49 ± 1[a] (47,[b] 53,[c] 56[d])	0.33 ± 0.03[a] (0.39[g])	25 ± 3[a]	34 ± 1[a]
2	Toluene	0.51–1.4	58 ± 1 (58[b])	0.39 ± 0.05	22 ± 3	32 ± 1
3	Ethylbenzene	0.50–1.2	59 ± 1	0.35 ± 0.03	25 ± 3	33 ± 2
4	Isopropylbenzene	0.40–1.2	55 ± 1 (57[e])	0.39 ± 0.04 (0.320[e])	19 ± 1	30 ± 1
5	*t*-Butylbenzene	0.40–1.2	60 ± 1	0.35 ± 0.03	23 ± 2	29 ± 1
6	Laurylbenzene	0.57–1.0	62 ± 1	0.43 ± 0.04	29 ± 2	38 ± 2
7	*o*-Xylene	0.49–1.2	68 ± 1	0.35 ± 0.05	27 ± 3	33 ± 2
8	*m*-Xylene	0.51–1.3	69 ± 1	0.41 ± 0.03	26 ± 2	34 ± 2
9	*p*-Xylene	0.50–1.3	69 ± 1 (66[b])	0.39 ± 0.04	28 ± 2	34 ± 2
10	Mesitylene	0.51–1.1	78 ± 1 (73[b])	0.57 ± 0.03	27 ± 1	37 ± 2
11	Durene	0.40–1.1	85 ± 1	0.60 ± 0.05	27 ± 2	36 ± 2
12	Hexamethylbenzene	0.30–0.70	106 ± 1 (102[f])	0.63 ± 0.03 (0.98 ± 0.05,[f] 0.85[h])	34 ± 1	37 ± 2
13	Naphthalene	0.60–2.2	48 ± 1	0.58 ± 0.04	18 ± 2	38 ± 2
14	α-Methylnaphthalene	0.60–1.6	55 ± 1	0.69 ± 0.08	19 ± 2	38 ± 2
15	β-Methylnaphthalene	0.80–2.0	54 ± 1	0.63 ± 0.05	19 ± 1	36 ± 2
16	2,3-Dimethylnaphthalene	0.30–1.2	58 ± 1	0.71 ± 0.03	22 ± 2	42 ± 2
17	2,6-Dimethylnaphthalene	0.50–1.0	59 ± 1	0.69 ± 0.04	22 ± 1	41 ± 2
18	Acenaphthene	0.31–1.2	58 ± 1	0.71 ± 0.05	20 ± 2	42 ± 1
19	1,2,3,6,7,8-Hexahydropyrene	0.32–0.59	69 ± 1	0.96 ± 0.09	22 ± 1	45 ± 4
20	Fluoranthene	0.30–0.66	49 ± 1	0.69 ± 0.09	19 ± 2	38 ± 2
21	Biphenyl	0.45–1.1	52 ± 1	0.57 ± 0.11	26 ± 2	35 ± 3
22	Fluorene	0.35–1.1	57 ± 1	0.42 ± 0.08	31 ± 5	39 ± 2
23	4,5,9,10-Tetrahydropyrene	0.36–1.3	69 ± 1	0.78 ± 0.05	25 ± 3	37 ± 2
24	*o*-Terphenyl	0.30–0.75	52 ± 2	1.0 ± 0.07	18 ± 2	31 ± 1
25	*m*-Terphenyl	0.30–0.55	56 ± 1	0.98 ± 0.08	19 ± 3	34 ± 1
26	Phenanthrene	0.51–1.2	48 ± 1	0.58 ± 0.07	25 ± 4	35 ± 4
27	Pyrene	0.20–0.35	43 ± 1	0.75 ± 0.07	20 ± 1	...[k]
28	Ferrocene	0.32–0.50	70 ± 1	0.59 ± 0.04	29 ± 3	35 ± 4
29	Cyclopentadiene	1.2–2.1	70 ± 1	...[i]	...[i]	58 ± 2
30	Isopropylcyclopentadiene	1.4–1.9	84 ± 2	...[i]	...[i]	78 ± 2
31	1-Methyl-1,3-butadiene	1.5–2.6	56 ± 2	0.30 ± 0.02	22 ± 2	64 ± 4
32	2-Methyl-1,3-butadiene	1.0–3.0	56 ± 2	0.27 ± 0.01	23 ± 1	64 ± 2
33	2,3-Dimethyl-1,3-butadiene	0.83–1.8	92 ± 5	0.47 ± 0.02	...[l]	...[l]
34	1,3-Cyclooctadiene	1.0–2.0	74 ± 3	0.29 ± 0.01	24 ± 2	77 ± 7
35	1,4-Hexadiene	1.3–2.5	68 ± 2	0.34 ± 0.01	21 ± 2	77 ± 4
36	*trans*, *trans*, *cis*-1,5,9-Cyclododecatriene	0.98–2.0	103 ± 2	0.47 ± 0.05	29 ± 2	76 ± 7
37	Cyclohexene	1.4–8.5	99 ± 2 (95[b])	0.21 ± 0.03	29 ± 2	81 ± 2

[a] Error limits with 95% confidence. [b] R. West, *J. Am. Chem. Soc.*, **81,** 1614 (1959). [c] T. Shimanouchi and Y. Ikeda, the 8th Discussion on Infrared and Raman Spectroscopy, Tokyo, Oct 1961. [d] C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60,** 1615 (1956). [e] S. Wada, *Bull. Chem. Soc. Japan*, **35,** 707 (1962). [f] 30°, ref 7. [g] 25°, ref 3b. [h] 20°: N. Fuson, P. Pineau, and M.-L. Josien, *J. Chim. Phys.*, **55,** 454 (1958). [i] π base was too unstable to obtain reproducible results. [j] Free OH vibration; $A = 11 \pm 1 \times 10^3$ l. mole^{-1} cm^{-2}, $\Delta\nu_{1/2} = 16 \pm 1$ cm^{-1}. [k] Owing to the poor solubility of pyrene in CCl_4, apparent intensity was to weak to obtain reliable values. [l] Very broad band.

since the lateral approach of a phenol molecule to the ring of hexamethylbenzene might be sterically hindered. This steric effect does not appear in monoalkylbenzene, since the phenol–laurylbenzene complex in Figure 5 fits the correlation line.[27] These results are in contradiction with those of Krueger and Mettee[4] who claimed that the K values of methanol–methylbenzene complexes are extremely sensitive to the steric effect of methyl groups. By neglecting the overlap of the bonded OH with the free OH absorption band in their analysis, the errors of the calculated K values are the more serious the weaker the hydrogen-bonding interaction becomes.

Figure 5 provides a clue to the meaning of the $-\Delta F$ *vs.* $\Delta\nu$ plot often discussed for the ordinary type of hydrogen bond with no success.[28,29] The $-\Delta F$ *vs.* $\Delta\nu$ relation depends strongly on the type of the π base. Polycondensed aromatics, alkylbenzenes including ferrocene, and monoolefins[27] form different groups of π bases as proton acceptors. Conjugated diolefins seem to behave as intermediate between alkylbenzenes and monoolefins. Although nonconjugated dienes

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(27) In the monoolefin series, a long alkyl chain attached to sp^2 carbon diminishes the complex formation constant K with phenol (Z. Yoshida and N. Ishibe, unpublished result). This suggests that, owing to their smaller π-electron density, the monoolefins are more sensitive to steric hindrance by alkyl groups.

(28) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84,** 3817 (1962).

(29) (a) G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14,** 1485 (1960); (b) T. Gramstad, *ibid.*, **15,** 1337 (1961); (c) E. Grunwald and W. C. Coburn, *J. Am. Chem. Soc.*, **80,** 1322 (1958).

Table II. Frequency Shifts $\Delta\nu_{OH}$ of Phenol due to Hydrogen Bonding with Some Heteroaromatics, Half-Widths $\Delta\nu^{b}_{1/2}$ of the Bonded OH Band, and Equilibrium Constants K of Hydrogen Bonding in Carbon Tetrachloride

No.	π base	$\Delta\nu_{OH}$, cm^{-1}	$\Delta\nu^{b}_{1/2}$, cm^{-1}	K (29°), l. mole^{-1}
38	Furan	48 ± 1[a]	51 ± 2[a]	0.34 ± 0.09[a]
39	2-Methylfuran	66 ± 1	49 ± 2	0.36 ± 0.09
40	2,5-Dimethylfuran	82.5 ± 1	57 ± 2	0.76 ± 0.07
41	Dibenzofuran	49.5 ± 1	72 ± 2	0.79 ± 0.06
42	Thiophene	52.5 ± 1	42 ± 2	0.38 ± 0.05
43	2-Methylthiophene	64 ± 1	50 ± 2	0.31 ± 0.09
44	2,5-Dimethylthiophene	74.5 ± 1	50 ± 2	0.40 ± 0.05
45	Dibenzothiophene	42 ± 1	38 ± 2	0.49 ± 0.05
46	N-Methylpyrrole	114 ± 2	68 ± 2	1.40 ± 0.20
47	N-Ethylcarbazole	61.5 ± 1	47 ± 2	1.16 ± 0.08
48	Tetrahydrofuran	295[b]		
49	Tetrahydrothiophene	262[b]		

[a] Average deviation from the mean. [b] Taken from E. Lippert and H. Prigge, *Ann.*, **659**, 81 (1962).

and trienes appear to belong to the conjugated diolefin group, they fit the monoolefin plot when $K/2$ or $K/3$ was taken to be the real equilibrium constant. In Figure 5, the points for the nonconjugated polyenes are based on the corrected K values. The experimental equation is $-\Delta F = a\Delta\nu + b$, where a and b differ from group to group. One intuitively expects that the term $a\Delta\nu$ will be related to $-\Delta H$ and b will correspond to $T\Delta S$, from the similarity in form of this experimental relation with the thermodynamic law, $-\Delta F = -\Delta H + T\Delta S$. A limited test suggested that this analogy holds. Table IV shows the values of a and b of the linear relationship in Figure 5. $\Delta S°$ values were estimated from b and $T = 302$°K.

The slopes are fairly constant and agree surprisingly well with the slope of the Badger-Bauger relation ($-\Delta H = 0.016\Delta\nu + 0.63 \pm 0.5$) determined recently by Joesten and Drago[28] for phenol-n-base adducts in CCl_4. Furthermore, the estimated $\Delta S°$ for the four groups of π bases also agreed with a limited number of experimental values reported by West.[30]

This consideration gives some support to the previous suggestion[2] that the entropy term has a determining importance for the stability of the hydrogen-bonded complex involving a π base. To account for such an entropy effect, a certain degree of freedom of movement of the proton donor molecule should be considered in the proposed configuration of this type of hydrogen-bonded complex, in which the proton donor X–H bond lies near the sixfold axis of benzene ring.[31,32]

Interesting information on the extent of conjugation in the π base can be obtained from the $-\Delta F$ *vs.* $\Delta\nu$ plots. Some examples are given later in this paper. The importance of charge transfer in this type of hydrogen bond interaction, as might be expected from the nonpolar character and high polarizability of the delocalized π electrons of the π bases,[33] has been demonstrated in the previous paper[2b] in terms of several pieces of indirect evidence based on spectral properties of the complexes. The same conclusion is obtained by use of the present data.[34]

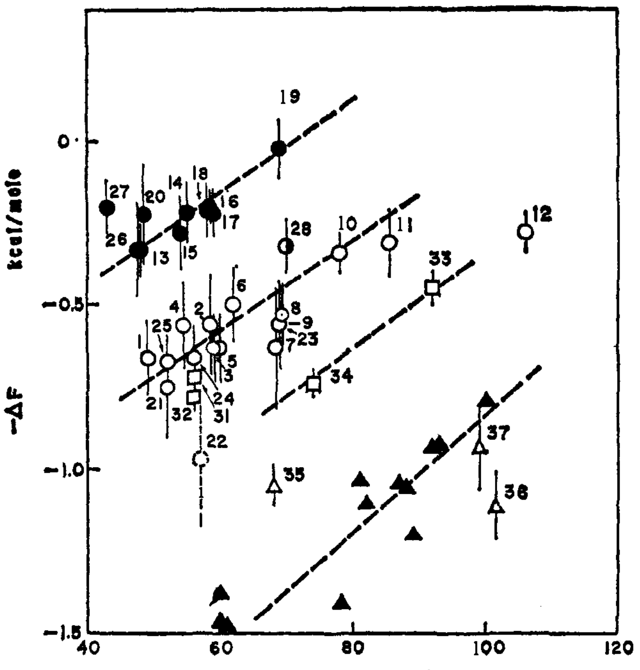

Figure 5. Plots of $-\Delta F$ *vs.* $\Delta\nu$ with phenol–aromatics and phenol–olefin complexes: ●, polyacene; ○, alkylbenzene; ◑, ferrocene; □, conjugated diolefin; △, monoolefin and nonconjugated polyolefin. The numbers correspond to π bases listed in Table I. The monoolefin line (—▲—) was taken from unpublished work of Z. Yoshida and N. Ishibe.

Phenol–Heteroaromatic Complexes

The OH stretching bands of phenol in the presence of an excess of heteroaromatics (Table II) were doublets without exception. This is consistent with the observation that the charge-transfer band of the thiophene–iodine complex is a singlet,[35] indicating the single donor character of these heteroaromatics. In view of the known fact that the proton magnetic resonance signal of chloroform is shifted toward higher fields by diluting gradually with furan and thiophene,[11] the observed single-bonded OH band corresponds to the interaction with the π-electron system of the heteroaromatic ring. A further indication of the nonexistence of O–H···n-electron type complex is obtained from the $-\Delta F$ *vs.* $\Delta\nu$ relation (see Figure 6). The values for furan, thiophene, and their methyl derivatives correlate with those for alkylbenzenes, while dibenzofuran and dibenzothiophene fit the regression line of polyacenes. This suggests that the furans and thiophenes act as π bases in hydrogen bonding.[36] The fact that the $-\Delta F$ *vs.* $\Delta\nu$ plots for the heteroaromatic π donors,

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(30) R. West, *Proc. Inter. Symp. Mol. Struct. Spectry., Tokyo*, D117 (1962).

(31) Nmr: (a) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957); (b) ref 3a.

(32) X-Ray: A. T. McPhail and G. A. Sim, *Chem. Commun.*, 124 (1965).

(33) L. N. Ferguson, ref 22, p 134.

(34) E. Ōsawa, Ph.D. Thesis, presented to the Faculty of Engineering, Kyoto University, 1965.

(35) J. E. Collin, *Bull. Soc. Roy. Sci. Liège*, **23**, 395 (1954).

(36) In contrast to our present results, Gramstad[9] reported the $\Delta\nu_{OH}$ of phenol in CCl_4 solution to be 103 and 113 cm^{-1}, respectively, and assigned them to the O–H···O interactions with furan and 2,5-dimethylfuran. We found no absorption at these frequencies. We have once observed additional ν^{b}_{OH} peaks at about 3350 and 3400 cm^{-1} when impure 2-methylfuran and 2,5-dimethylfuran were used as the proton acceptors. However, after purifying the furans through preparative vpc, these bands disappeared.

Table III. Frequency Shifts $\Delta\nu_{OH}$ of Phenol Due to Hydrogen Bonding with Fulvenes and Azulenes, Half-Widths $\Delta\nu^{b}{}_{1/2}$ and Molar Absorbances A^b of Bonded OH Bands, and Equilibrium Constants of Hydrogen Bonding in Carbon Tetrachloride

No.	π base R₁	π base R₂		$\Delta\nu_{OH}$, cm^{-1}	$\Delta\nu^{b}{}_{1/2}$, cm^{-1}	A^b, l. mole^{-1} cm^{-2}	$K^{29°}$, l. mole^{-1}
				6,6-Dialkylfulvenes, $C_5H_4{=}CR_1R_2$			
50	CH_3	CH_3		86 ± 1[a]	67 ± 3[a]	23 ± 2[a] × 10³	0.74 ± 0.07[a]
51	CH_3	C_2H_5		88 ± 1	70 ± 8	18 ± 3	0.70 ± 0.07
52	CH_3	n-C_3H_7		87 ± 1	65 ± 4	23 ± 2	0.88 ± 0.05
53	CH_3	i-C_3H_7		87 ± 1	66 ± 5	19 ± 1	0.96 ± 0.07
54	CH_3	$CH{=}C(CH_3)_2$		(104 ± 2)[b]	(83 ± 7)[b]	(20 ± 1)[b]	(1.1 ± 0.04)[b]
55	$(CH_2)_5$			(90 ± 2)[c]	(68 ± 2)[c]	(23 ± 2)[c]	(0.76 ± 0.10)[c]
56	i-C_4H_9	i-C_4H_9		90 ± 1	70 ± 1	19 ± 1	1.1 ± 0.04
				Arylfulvenes, $C_5H_4{=}CR_1R_2$			
57	CH_3	C_6H_5	α	57 ± 3	47± 3	19 ± 1	0.30 ± 0.15
			β	87 ± 3	79 ± 4		1.0 ± 0.5
58	CH_3	$C_6H_4CH(p)$	α	63 ± 2	45 ± 4	22 ± 1	0.21 ± 0.03
			β	83 ± 4	81 ± 2		1.0 ± 0.1
59	CH_3	$C_6H_4Cl(p)$	α	(22 ± 1)	(35 ± 5)	20 ± 1	(0.1 ± 0.05)
			β	80 ± 1	82 ± 3		0.79 ± 0.06
60	CH_3	$C_6H_4NO(m)$		71 ± 1[d]	81 ± 1	19 ± 2	3.7 ± 1.0[d]
61	CH_3	α-$C_{10}H_7$	α	50 ± 2	48 ± 3	19 ± 1	0.45 ± 0.06
			β	94 ± 2	94 ± 5		0.86 ± 0.05
62	C_6H_5	C_6H_5	α	51 ± 1	36 ± 3	23 ± 3	0.25 ± 0.08
			β	80 ±2	78 ± 7		0.79 ± 0.13
63	H	α-Furyl		78 ± 2	(78 ± 3)	25 ± 2	0.52 ± 0.05
				Azulenes			
64	Azulene		α	45 ± 2	58 ± 3	18 ± 2	0.19 ± 0.04
			β	84 ± 3	74 ± 5		0.53 ± 0.13
65	4,6,8-Trimethyl-azulene		α	79 ± 3	68 ± 6	21 ± 3	0.31 ± 0.04
			β	116 ± 3	83 ± 6		1.1 ± 0.04
66	4,8-Dimethyl-6-*t*-butylazulene		α	72 ± 2	66 ± 5	20 ± 3	0.46 ± 0.03
			β	115 ± 2	75 ± 5		1.4 ± 0.17
67	Guaiazulene		α	62 ± 2	59 ± 2	23 ± 4	0.25 ± 0.04
			β	105 ± 2	80 ± 6		0.87 ± 0.09
68	Nitrobenzene			66 ± 2[d,e]	83 ± 2	20 ± 2	3.5 ± 1.5[d]

[a] Mean deviation from the average. [b] Inaccurate due to overlap with the third extremely broad absorption band. [c] Inaccurate due to instability of 6,6-cyclopentamethylenefulvene. [d] Sensitive to variation of π-base concentration. The figures were obtained by extrapolating to infinite dilutions. *Cf.* ref 23 and 31. [e] Lit.[31] 67 cm⁻¹.

Table IV. Slope *a* and Intercept *b* of the Experimental Lines in Figure 5

Group of π base	*a*, kcal mole⁻¹ cm	*b*, kcal mole⁻¹	ΔS°, cal deg⁻¹ mole⁻¹ Estd	ΔS°, cal deg⁻¹ mole⁻¹ Obsd[a]
Polycondensed aromatics (A)	0.013	−0.92	2–3	1–3
Alkylbenzenes and ferrocene (B)	0.014	−1.4	4–6	4–5
Conjugated diolefins (C)	(0.015)	−1.8	5–7	7
Monoolefins and nonconjugated polyolefins (D)	0.018	−2.7	8–10	6–9

[a] Reference 30; Z. Yoshida and N. Ishibe, unpublished results.

N-methylpyrrole and N-ethylcarbazole,[37] were on the alkylbenzene line and the polyaceneline, respectively, agrees well with our theory.

The Δν for furan was the same as that for benzene. This value will be the result of two effects of opposite sign: shift-increasing effects such as the negative net charge on the ring carbon (−0.017 at C-2 and −0.083 at C-3) and the low localization energy of π electrons at C-2[39] on one hand, and shift-decreasing effects such as a positive net charge on the oxygen atom (+0.200)[39] and contribution from the π-electron delocalization[40] on the other hand. The introduction of a methyl group in the furan ring should pronounce the shift-increasing and diminish the shift-decreasing factors. The observation of the pronounced increase of Δν with the number of methyl groups on the furan ring compared with the "nonpolar" benzene series is shown in Figure 7.

The effect of a methyl group on Δν in the thiophene ring goes parallel with benzene. Slightly higher Δν values for thiophenes will be due to its smaller ring. Although there has been some controversy as to the possibility of sulfur 3d orbital participating in the cyclic conjugation in thiophene,[38,39,41] the similarity between methyl-substituted thiophenes and benzenes as proton acceptors supports the dπ-pπ interaction in thiophene. Through this interaction, the cyclic conjugation is enhanced so that the ring becomes effectively nonpolar. This is in good agreement with the recent evaluation of the relative magnitude of the induced ring current of heteroaromatics: thiophene retains 75% of the ring current of benzene, whereas furan (46%) is certainly less aromatic.[40]

It should be noted that N-methylpyrrole and N-ethylcarbazole are remarkably strong bases, as strong as hexamethylbenzene (12) and 1,2,3,6,7,8-hexahydropyrene (19). Their high basicity as π donors will be the result of an effective diminution of positive charge[39]

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(37) They act as π donors because they fail to undergo Diels–Alder condensations[38] and protonate only on the ring carbon: Y. Chiang and E. B. Whipple, *J. Am. Chem. Soc.*, **85**, 2763 (1963).

(38) A. Albert, "Heterocyclic Chemistry, An Introduction," Athlone Press, London, 1959.

(39) D. S. Sappenfield and M. Kreevoy, *Tetrahedron Suppl.*, **2**, 157 (1963); *cf.* B. Bak, *Bol. Sci. Fac. Chim. Ind. Bologna*, **21**, 8 (1963).

(40) J. A. Elvidge, *Chem. Commun.*, 160 (1965).

(41) Comment of R. D. Brown in ref 37.

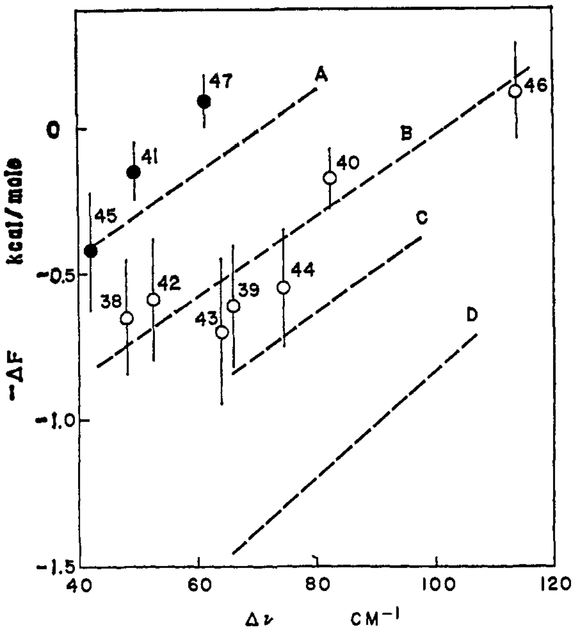
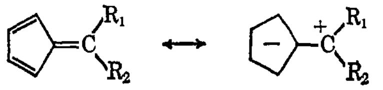


Figure 6. ΔF *vs.* $\Delta\nu$ plot with phenol–heteroaromatic adducts in carbon tetrachloride solution. Numbers correspond to those listed in Table II: (A) polyacene line, (B) alkylbenzene line, (C) conjugated diolefin line, (D) monoolefin line (*cf.* Figure 5).

on the nitrogen atom through inductive as well as hyperconjugative[42] effects of methyl or ethyl groups attached to it.

Phenol–Fulvene Complexes

Alkylfulvenes. As expected, 6,6-dialkylfulvenes proved to be stronger proton acceptors than alkylbenzenes, since both $-\Delta F$ and $\Delta\nu$ for the dialkylfulvenes were comparable with those of "tetramethylbenzenes" (see Figure 8). The dialkylfulvenes are formally the isomers of "dialkylbenzenes." It is interesting to note that, on changing the substituents at C-6 from methyl to ethyl, propyl, and butyl, K increased while $\Delta\nu$ remained essentially unchanged. If the olefinic structure **1** is greatly predominant in fulvenes as can be deduced from dipole moment data,[7] both K and $\Delta\nu$ should have been increased by the substituent effects of R_1 and R_2. This was so for benzenoid and olefinic π bases. This discrepancy can be explained by assuming that the formation of a hydrogen-bonded π complex with alkylfulvene polarizes the molecule in the sense of a structure **2**. This effect becomes more pronounced as the stabilizing influence of the alkyl groups is enhanced. Reasonably this would follow the normal order for inductive effects. The constancy of $\Delta\nu$ would be the result of compensation of the $\Delta\nu$-decreasing effect of the enhanced 6π cyclic conjugation, on one hand, and the $\Delta\nu$-increasing effect of a growing negative charge on the ring, on the other. The increase of K would be the result of an increase of the ΔS term caused by the cyclic conjugation effect. The fact that the $-\Delta F$ *vs.* $\Delta\nu$ plots for the alkylfulvenes fall close to the "alkylbenzene line" offers a strong support for our arguments.



1 2

Arylfulvenes. The α and β bands of the bonded OH absorption (Table III) were assigned to the OH bonded to the aryl ring (**3**) and the fulvene ring (**4**), respectively, on the following basis.

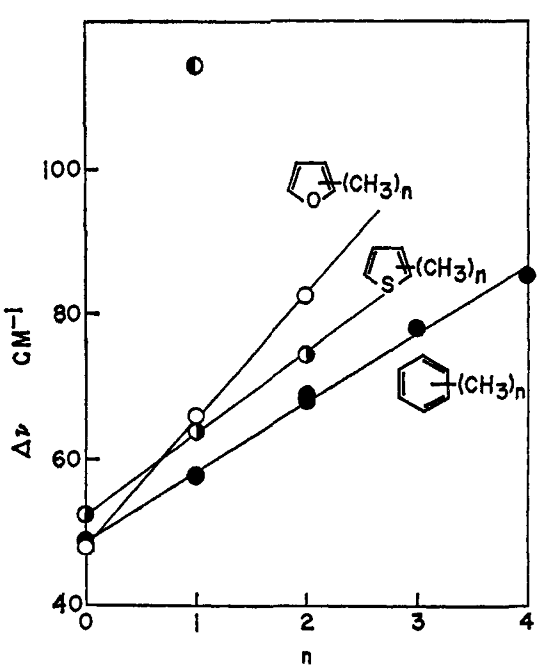


Figure 7. Dependence of $\Delta\nu$ on the number of methyl groups on furan (○), thiophene (◑), and benzene (●) rings; ◐, N-methylpyrrole.

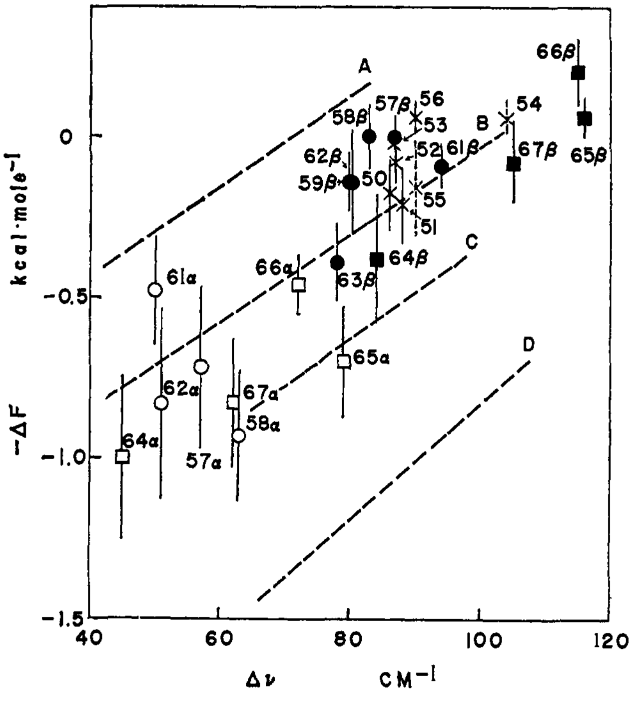


Figure 8. ΔF *vs.* $\Delta\nu$ plot with phenol–fulvene and phenol–azulenes adducts in carbon tetrachloride solution. Numbers correspond to those listed in Table III: ×, alkylfulvenes; ○ and ●, arylfulvenes; □ and ■, azulenes. (A) polyacene line, (B) alkylbenzene line, (C) conjugated diolefin line, (D) monoolefin line.

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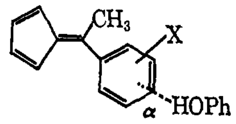
[42] The effect of hyperconjugation on the hydrogen bond shift has been observed: L. F. Ferstandig, *Tetrahedron*, 20, 1367 (1964).



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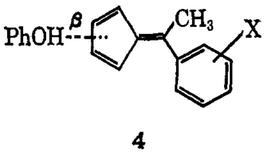


4

(1) The frequencies of the α bands are close to those of the OH bonded to the corresponding aryl hydrocarbons, while the position of the β bands corresponded well to those of alkylfulvenes.

(2) The effects of a substituent of the aryl ring on the frequencies of the α band can be reasonably interpreted in terms of this assignment. The β bands are virtually insensitive.

(3) From the $-\Delta F$ *vs.* $\Delta\nu$ plots (Figure 8), the plots for the α bands fell near the "alkylbenzene line." The point for 6-methyl-6-(α-naphthyl)fulvene (61a) fell near the "polyacene line," which indicates that this point corresponds to the O-H···naphthyl ring bonding. The plots for the β bands correspond well to those of the alkylfulvenes, and again fell close to the "alkylbenzene line."

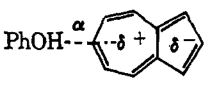
The splitting of the bonded OH band will be concerned with the noncoplanarity of the aryl group and the fulvene ring owing to the hydrogen interaction at methyl and C-2′. The angle of deviation has been estimated to be about 30° from ultraviolet data.[18] When the almost coplanar 6-(α-furyl)fulvene (63) was used as the proton acceptor, the α band virtually disappeared.

Azulenes. The assumptions described in the Experimental Section to calculate K_α and K_β for the hydrogen bonding of phenol with azulenes (values listed in Table III) do not seem very reasonable, since an intramolecular migration of phenol within the plane of the azulene molecule will be possible in such a weak interaction.

$$\mathrm{PhOH}\cdot\alpha \rightleftharpoons \mathrm{PhOH}\cdot\beta$$

However, from the over-all equilibrium constants and $\Delta\nu_\alpha$ and $\Delta\nu_\beta$ values which are significant, it can be concluded that the azulenes are very strong proton acceptors, in agreement with our expectation. The over-all K (1.4–1.9 l. mole^{-1}) and $\Delta\nu_\beta$ (116 cm^{-1}) for 4,6,8-trialkylazulenes (65 and 66) are the largest of the π bases studied in this work.[43]

The assignment of the α and β band is difficult for this series, since the effect of a limited number of alkyl substituents on K and $\Delta\nu$ appears essentially similar for both bands. However, from the fact that the $-\Delta F$ *vs.* $\Delta\nu$ plots were all near the "alkylbenzene line," we might tentatively assign the α band to the OH bonded to the seven-membered ring (**5**) and the β band to the OH bonded to the five-membered ring (**6**).



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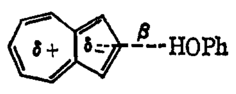

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It is rather unusual that a weak hydrogen-bonding interaction between phenol and fulvenes or azulenes seems to cause the prevalence of the polar structures like **2**, **5**, and **6**. In an isolated unperturbed state the importance of the structure **2** has been estimated to be less than 10% on the basis of dipole moment data.[7] This is consistent with the fact that the ring proton coupling constants of some simple fulvenes are in close agreement with those of dienes.[44] The same is true for the ground state of azulenes. The dipole moments are rather low,[45] and the high diamagnetic susceptibility exaltation, as measured by shielding constants derived from nmr solvent shifts, has been attributed to its character as a monocyclic 10π-electron system.[46] Therefore, one might conclude that the π electrons of these nonbenzenoid aromatics are unusually easily polarized by a weak perturbation, such as hydrogen bonding.[47]

Acknowledgment. Hearty thanks are due to Dr. Werner Koch for reading the manuscript and discussion. The authors are grateful to Messrs. N. Ishibe, T. Kobayashi, and T. Kato for their experimental assistance and suggestions.

(43) The lowest frequency ever reported for the stretching absorption of OH bonded with a π electron is 3.32 μ (about 3010 cm^{-1}) for the intramolecular hydrogen bonding in 2-(1-hydroxydicyanovinyl)diazocyclopentadiene: D. J. Cram and R. D. Partos, *J. Am. Chem. Soc.*, **85**, 1273 (1963).

(44) W. B. Smith and B. A. Shoulders, *ibid.*, **86**, 3118 (1964).

(45) A. G. Anderson, Jr., and B. M. Steckler, *ibid.*, **81**, 4941 (1959).

(46) D. J. Bertelli and C. Golino, *J. Org. Chem.*, 30, 368 (1965).

(47) The authors are indebted to Professor Robert West, the University of Wisconsin, for this suggestion.