Analysis of the Data.—The curves of Figs. 1 and 2 indicate that interaction occurs between the ferric chloride solution and the α-glucose solution, and that the presence of the ferric chloride increases the rate of mutarotation of the α-glucose. Our initial experiments, involving spectrophotometric studies of solutions of glucose and ferric ion in equilibrium, and utilizing the limiting logarithm method described by Bent and French[4] and the method of continuous variations as modified by Vosburgh and Cooper,[5] indicated the formation of at least one complex containing iron and glucose in equimolar amounts.

Since the conditions under which data for Figs. 1 and 2 were obtained were the same (with the exception of the variation in the concentration of the ferric chloride solution), only Fig. 2 will be considered in the following discussion. The upper curve of Fig. 2 shows the rate of mutarotation of the α-glucose in 0.1 *M* hydrochloric acid with no ferric chloride added. The first value shown, obtained five minutes after solid α-glucose was added to the hydrochloric acid, was 60.2°. As the curve indicates, no appreciable change in the rotation was observed after a period of approximately sixty minutes. The lower curve in Fig. 2 shows the rate of mutarotation of α-glucose in 0.1 *M* hydrochloric acid in the presence of 0.4 *M* ferric chloride. Again, the initial reading was made five minutes after the solid α-glucose was added to the solution. This reading (53.50) is appreciably lower than the previous reading. This curve levels off much more rapidly than the other, the observed rotation becoming constant after a period of approximately twenty-five minutes.

In any complex with iron(III) and glucose one might expect the ferric ion to be attached to the glucose molecule through the carbonyl oxygen. There is no reason to assume that this complexing should destroy the optical activity of the glucose molecule. It is known that an equilibrium exists between the α- and β-forms of glucose in solution. If the ferric ion were to combine with the α-form of glucose, one would expect the rate of mutarotation to decrease. Conversely, if the ferric ion were to combine with the β-form, the rate should increase. Since, in the case cited, the addition of the ferric ion results in an increased rate of mutarotation, it is concluded that the ferric ion complexes with the β- rather than the α-form of glucose.

This conclusion is supported by the slightly lower equilibrium optical rotation of the solution containing the ferric chloride. The difference between the two equilibrium values is of the order of the experimental error; however, approximately the same difference is noted for both series of runs. If the complex were formed with the α-rather than the β-form of glucose, one would expect the measured (*i. e.*, total) rotation at equilibrium to be greater than that for pure glucose solutions, which is precisely the opposite of the observed effect. Thus, assuming that the formation of the complex does not destroy the optical activity of the glucose molecule, one may say that the iron complexes preferably with the β-form.

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[4] Bent and French, This Journal, **63**, 568 (1941).

[5] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

Calculation of Resonance Energies

By J. L. Franklin

It has been shown that the heat of formation and free energy of formation of organic molecules are additive functions of characteristic group equivalents.[1,2] Since resonance energy is calculated as the difference between the heat of formation of a molecule and that of the corresponding structure assuming no resonance, it follows that the method of group equivalents can be used to calculate resonance energies. Further, this method automatically allows for steric effects and hyperconjugation.

Resonance affects electronic levels primarily and rotational and vibrational levels secondarily. Assuming no low-lying excited electronic levels, the electronic partition function is simply $e^{-E/RT}$ and the electronic entropy is zero. Consequently, a change in electronic energy due to resonance will have no effect on entropy. The rotational and vibrational entropy of a resonating molecule will be different from that of the corresponding hypothetical non-resonating molecule because of changes in bond distance, symmetry, and force constants. These might be expected to decrease slightly the entropy of the resonating molecule. It is observed, however, that resonance energies calculated from heats of formation and from free energies of formation are almost identical and vary but little with temperature so it might be concluded that the latter effects are small. Consequently, resonance energies may be calculated by the method of group equivalents from

TABLE I

CALCULATION OF RESONANCE ENERGY OF BENZENE

	ΔH_f^0	ΔF_f^0
$3\,{}_{\mathrm{H}}^{\diagdown}C{=}C_{\mathrm{H}}^{\diagup}$ (*cis*)	56.6	71.8
C_6 ring correction	−0.5	−6.4
Symmetry correction ($RT \ln \sigma$)	...	1.5
ΔH_f^0 or ΔF_f^0 for non-resonating structure	56.1	66.9
ΔH_f^0 or ΔF_f^0 for C_6H_6 from API[3] tables	19.8	31.0
Resonance energy	36.3	35.9

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[1] Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

[2] Bremner and Thomas, *Trans. Faraday Soc.*, **44**, 338 (1948).

[3] Selected Values of Properties of the Hydrocarbons, API Project 44, National Bureau of Standards Circular C461, Nov., 1947.

either heats of formation or free energies of formation, as illustrated for benzene in Table I.

The results are in excellent agreement with the value calculated from heats of hydrogenation. Table II compares resonance energies of several compounds computed from group equivalents and heats of formation with values obtained from bond energies, heats of hydrogenation, and heats of combustion.

TABLE II

RESONANCE ENERGIES

	Pauling[4] Bond energies	Wheland[5] Hydrogenation	Wheland[5] Combustion	This study group equivalents
Benzene	39	36.0	41	36
Toluene	..	...	41	35
Ethylbenzene	..	35.2	43	35
o-Xylene	..	35.2	44	36
Mesitylene	..	33.1	50	34
Styrene	7^{a}	36.7	51	37
Phenylacetylene	10^{a}	...	52	35
Phenol	7^{a}	...	50	37
Aniline	6^{a}	...	51	39
Acetophenone	7^{a}	...	54	37
Benzoic acid	4^{b}	...	67^{c}	2^{b}
Benzaldehyde	4^{a}	...	47	32
Diphenyl	8^{a}	...	91	75
Naphthalene	75	...	77	62
Anthracene	105	...	116	87
Phthalic anhydride	..	...	..	52
1,3-Butadiene	..	3.5	..	3.2
1,4-Diphenyl-1,3-butadiene	..	10.7^{a}	..	5.2^{a}
Stilbene	15^{a}	79	101	5.9^{a}
Benzoquinone	..	...	16	7.0
Furan	23	17.2	24	23
Thiophen	31	...	29	31
Pyrrole	31	...	24	27
Urea	37	...	41	38
Acetic acid (monomer)	28	...	25	22
Acetic anhydride	..	...	41	29
Ethyl acetate	24	...	25	18
Formamide	21	...	20	17
Acetamide	21	...	25	21
Urea	37	...	41	38

[a] Resonance energy in excess of that of the aromatic nucleus. [b] Resonance energy in excess of that of the aromatic nucleus and COOH Group. [c] Corrected to the monomer.

It will be observed that there is excellent agreement between resonance energies calculated from heats of hydrogenation and those calculated from group equivalents and heats of formation even when the heats of formation are obtained from heats of combustion. We may conclude therefore that the method of group equivalents gives resonance energies of satisfactory accuracy. There are, however, quite large discrepancies in many instances between resonance energies calculated from group equivalents or heats of hydrogenation and those based entirely upon heats of combustion or bond energies. Since the latter do not in most instances include allowances for the effect of neighboring groups, they may be considered to be less accurate than the former.

It is of interest to note that resonance energies calculated by the method of group equivalents for such compounds as phenol, aniline, benzoic acid, benzaldehyde and phenylacetylene show resonance energies that are very little different from those of benzene. Although the resonance energies of these compounds are in general slightly higher than that of benzene, they are in most cases smaller than the values given by Pauling[4] and Wheland.[5] Small resonance energy between the benzene ring and substituent does not necessarily indicate small resonance interaction since it can be shown that the resonance energy may be quite insensitive to the extent of interaction. In contrast, the spectra, dipole moments and chemical activity of monosubstituted benzenes can be shown to be quite sensitive to the extent of interaction.[6] Another example is the quite large effect on chemical activity resulting from hyperconjugation in mono-olefins even though the heats of hydrogenation may differ by only a few kilocalories.

As a consequence of the fact that the entropy of a molecule is not affected by resonance as discussed above, the resonance energy of a compound calculated from heats of formation at 298°K. can be employed with the aid of group equivalents at various temperatures to calculate the free energy of formation at those temperatures. Table III compares the free energies of several compounds calculated by this method with measured values.

TABLE III

FREE ENERGIES CALCULATED WITH THE AID OF RESONANCE ENERGIES

	ΔF_f^0 298°K. Measured	ΔF_f^0 298°K. Calculated	ΔF_f^0 1000°K. Measured	ΔF_f^0 1000°K. Calculated
Benzene	31.0	30.6	62.3	63.4
Toluene	29.2	29.0	76.3	77.7
Mesitylene	28.2	28.8	113.0	115.6
Styrene	51.1	50.0	93.9	93.1
p-Methylstyrene	50.2	49.6	111.0	111.0
Naphthalene	50.4	52.0	....	....
Anthracene	72.4	74.1	....	....
1,3-Butadiene	36.4	35.5	62.8	60.3
Isoprene	34.9	33.7	78.9	76.0
Thiophene	27.6	25.7	....	....
Phenol	− 6.3	− 4.9	....	....
Aniline	39.5	39.5	....	....
Urea	−42.5	−46.0	....	....
Acetic acid	−91.2	−92.4	−58.5	−61.9
Ethyl acetate	−77.8	−74.6	....	....

The agreement is quite good in most instances. The discrepancies with urea and ethyl acetate,

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[4] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[5] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

[6] Matsen, THIS JOURNAL, in press.

although rather large, are probably well within the accuracy of the data. It should be borne in mind that certain of the "measured" free energy values given actually represent results that were obtained on materials in the solid or liquid phase, and free energies of vaporization of considerable magnitude had to be estimated in order to convert the values to the gas phase where resonance energies are applicable. These estimates introduce an uncertainty of at least 2 kilocalories in some instances.

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Tetra-2-naphthylsilane

BY HENRY GILMAN AND CECIL G. BRANNEN

In connection with studies on steric hindrance in arylsilanes, we have synthesized tetra-2-naphthylsilane. This is of interest because of a generalized comment[1a] that four naphthyl or tolyl groups can be bonded to silicon. Four tolyl groups have been attached to silicon,[1b] but none of the compounds reported has an *ortho* substituent, which is of most significance in steric studies. There appears to be no reference concerning tetra-*o*-tolyl- or any tetranaphthyl-silane. Furthermore, experiments designed to bond four *o*-tolyl radicals to silicon have demonstrated[2] that the fourth group is introduced with difficulty.

We have found that tetra-2-naphthylsilane can be easily prepared by treating silicon tetrachloride, ethyl silicate, or trichlorosilane, respectively, with 2-naphthyllithium. The reactions involved in the preparation from trichlorosilane possibly proceed[3] through the formation of tri-2-naphthylsilane

$$3RLi + Cl_3SiH \longrightarrow R_3SiH + 3LiCl \qquad (1)$$

$$R_3SiH + RLi \longrightarrow R_4Si + LiH \qquad (2)$$

2-Naphthyllithium was made both by the direct method[4] from 2-bromonaphthalene and lithium metal and by halogen-metal interconversion[5] of 2-bromonaphthalene with *n*-butyllithium. The former method introduces colored impurities into the product which are difficult to eliminate by the ordinary techniques, while the latter method introduces the coupled product, 2,2′-binaphthyl, which is extraordinarily difficult to remove completely. Higher yields were obtained by treating silicon tetrachloride with 2-naphthyllithium prepared by the direct method and purifying the product by chromatography.

Preliminary experiments indicate that the preparation of tetra-1-naphthylsilane proceeds with considerable difficulty, probably largely because of steric hindrance.

Experimental

All temperatures are uncorrected unless otherwise noted.

Tetra-2-naphthylsilane: (a) **From Silicon Tetrachloride and 2-Naphthyllithium Made by the Direct Method.**—A 0.39 *N* solution of 2-naphthyllithium in ether was made from 10 g. (0.048 mole) of 2-bromonaphthalene[6] and 7 g. (0.1 g. atom) of lithium by the usual method, the yield (96%) being determined by acid titration.[7] Two grams (0.018 mole) of silicon tetrachloride in about 50 ml. of dry ether was added to the organolithium reagent with stirring. After refluxing for ten minutes the mixture was poured into dilute hydrochloric acid, the inorganic salts removed by extraction, and the organic layer steam-distilled. The residue was extracted with about 400 ml. of petroleum ether (b. p. 60–80°) and this extract was poured through a 4 × 20 cm. column of alumina.[8] The colored material was not eluted after development with 1 l. of solvent. The eluant was reduced to a small volume to obtain 5.1 g. (81%) of the pure silane, m. p. 216–217° (cor.).

Anal.[9] Calcd. for $C_{40}H_{28}Si$: Si, 5.22. Found: Si, 5.29, 5.20.

(b) **From Silicon Tetrachloride and 2-Naphthyllithium Made by Halogen-Metal Interconversion.**—To a solution of 10 g. (0.048 mole) of 2-bromonaphthalene, m. p. 57–58°, in 50 ml. of dry ether was added 0.048 mole of *n*-butyllithium[10] in 46 ml. of ether keeping the internal temperature at 5°. After stirring for fifteen minutes, 1.5 g. (0.0088 mole) of silicon tetrachloride in 15 ml. of ether was added dropwise maintaining the temperature at 5°. Color Test I[11] was positive even after stirring for two hours at 5° followed by refluxing thirty minutes. The mixture was poured into dilute hydrochloric acid; the organic layer was extracted with water and steam-distilled. The residue was extracted with petroleum ether (b. p. 60–80°). In four crops, 2.40 g. (51%) of the crude silane, m. p. 202–205°, was isolated. Recrystallization from ethanol–ethyl acetate (1:1) gave 2.10 g. (42%) of the pure silane, m. p. 216–217° (cor.).

(c) **From Ethyl Silicate.**—An ethereal solution of 20.7 g. (0.1 mole) of 2-bromonaphthalene and 0.1 mole of *n*-butyllithium were mixed under the usual conditions[5] at 5°. After stirring for ten minutes, 1.9 g. (0.009 mole) of ethyl silicate, b. p. 164° at 740 mm., in 20 ml. of dry ether was added dropwise and the mixture refluxed for fifteen hours. The mixture was worked up as in (b) using the same solvent for crystallization. 2,2′-Binaphthyl, 0.40 g. (6%), melting point and mixed melting point with an authentic specimen, 188–189° (cor.), separated first; then came an impure fraction, m. p. 150–160°; followed by 1.90 g. (40%) of the crude silane, m. p. 203–205°. Recrystallization of the crude silane gave 1.2 g. of material, m. p. 216–217° (cor.), which showed no depression when mixed with the material from (a).

Chromatographic adsorption of the petroleum ether extract failed to achieve a separation. Fractional crystallization of the solid present in the eluant showed this material to contain binaphthyl and the silane.

(d) **From Trichlorosilane.**—2-Naphthyllithium was made in the same manner as in (b) using the same quanti-

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[1] (a) Burkhard, Rochow, Booth, and Hartt, *Chem. Reviews*, **41**, 105 (1947); (b) Polis, *Ber.*, **18**, 1540 (1885).

[2] Unpublished studies by Dr. G. N. R. Smart.

[3] Gilman and Massie, THIS JOURNAL, **68**, 1128 (1946); Meals, *ibid.*, **68**, 1880 (1946); Gilman and Melvin, *ibid.*, **71**, 4050 (1949).

[4] Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932).

[5] Gilman and Moore, *ibid.*, **62**, 1843 (1940).

[6] Prepared in 55% yield in essential accordance with the directions of Newman and Wise, *ibid.*, **63**, 2847 (1941).

[7] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923).

[8] Fisher Scientific Company, 80–200 mesh.

[9] See Gilman, Hofferth, Dunn and Melvin, *ibid.*, **72**, in press (1950).

[10] Gilman, Beel, Brannen, Bullock, Dunn and Miller, *ibid.*, **71**, 1499 (1949).

[11] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).