notic properties of a barbituric acid with a 5-alkyl substituent containing a nitro group, it was thought to be of interest to prepare the barbituric acid from the above compound.

Considerable difficulty was experienced in bringing about the condensation between urea and ethyl ethyl-(1-methyl-1-nitroethyl)-malonate. The desired compound was finally obtained in 9% yield using a modification of a procedure described by McElvain and Goese.[2]

The pharmacological properties of the sodium salt of the compound were studied by Dr. J. N. Spencer of the Pharmacology Department of this Laboratory. He reports the following properties.

Intraperitoneal LD_{50} (mice)	360 mg./kg.
Oral LD_{50} (mice)	490 mg./kg.
Hypnotic dose (ED_{50}) (intraperitoneal in mice)	110 mg./kg.
No hypnotic action observed following oral administration in mice.	

Experimental

5-Ethyl-5-(1-methyl-1-nitroethyl)-barbituric Acid.—To a mixture of 4.8 g. (0.08 mole) of urea, 11 g. (0.04 mole) of ethyl ethyl-(1-methyl-1-nitroethyl)-malonate, and 100 ml. of dry *t*-butyl alcohol was added 0.5 g. of sodium methoxide. The alcohol was distilled from the stirred mixture at about 30 ml. per hour and fresh *t*-butyl alcohol was added continuously at the same rate. One-half gram portions of sodium methoxide were added every hour until 3.5 g. had been added. One hour after the last portion of sodium methoxide had been added, the *t*-butyl alcohol was distilled under reduced pressure. The residue was cooled, 100 ml. of water was added, and, after a short period of stirring, the water was extracted with 50 ml. of ether. Acidification of the water with concd. hydrochloric acid gave 0.9 g. of white ppt., m. p. 233–237°. Recrystallization from ethanol raised the m. p. (cor.) to 238–240° (dec.).

Anal. Calcd. for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.27. Found: C, 44.55; H, 5.46; N, 17.00.

McElvain and Goese[2] had used sodium *t*-butoxide as a catalyst. In the reaction reported the more readily available sodium methoxide was found to give equally good results.

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[2] S. M. McElvain and M. A. Goese, THIS JOURNAL, **65**, 2226 (1943).

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The Resonance Energy of Benzene

BY DONALD F. HORNIG

Only a small displacement of the carbon atoms is necessary to distort a normal benzene molecule with 1.39 Å. C–C bonds to a configuration where C–C bonds are alternately 1.34 and 1.54 Å.; *i.e.*, the configuration represented by a single Kekulé structure without resonance. Since the displacements are small, the energy expended in distorting the molecule can be obtained from the force constants derived from the vibrational spectrum. If, as is sometimes assumed, the bond length is a sufficient criterion of bond type, this energy might be expected to equal the resonance energy.

Since the C–H distance and H–C–C angle of Kekulé benzene are the same as those of benzene, the distortion involves only the two symmetry coordinates[1]

$$S_1 = (1/\sqrt{6})(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$$

$$S_{14} = (1/\sqrt{6})(r_1 - r_2 + r_3 - r_4 + r_5 - r_6)$$

whose forms are illustrated in Fig. 1. The *r*'s are the changes in the C–C bond lengths. The force constants corresponding to these symmetry coordinates have been designated Λ_1 and Λ_2 by Crawford and Miller[1] who found that $\Lambda_1 = 7.83 \times 10^5$ dyne/cm. Inserting the frequencies of the B_{2u} vibrations obtained by Mair and Hornig[2] (Table I) into the equations of Crawford and Miller, two possible sets of force constants for the B_{2u} species are obtained. They are given in Table II.

TABLE I

FREQUENCY OF B_{2u} VIBRATIONS IN BENZENE

Compound	ν_{14}, cm.$^{-1}$	ν_{15}, cm.$^{-1}$
C_6H_6	1311	1147
C_6D_6	1287	825

TABLE II

B_{2u} FORCE CONSTANTS

	Force constant $\times 10^5$ dyne/cm.	
C–H bending, Γ_2	0.828	0.828
C–C stretching, Λ_2	4.361	3.926
Interaction, μ_2	0.667	0.290

The C–H bending force constant, Γ_2, is essentially identical with those obtained for other symmetry species by Crawford and Miller, 0.83, 0.87 and 0.85×10^5 dynes/cm., agreeing better than the value 0.95×10^5 dynes/cm. obtained by them for the B_{2u} species, using the earlier frequency assignment of Ingold and co-workers.[3] It is difficult to choose between the alternative values for Λ_2 or μ_2 on physical grounds but fortunately they are so nearly the same that the choice does not affect the conclusions markedly. Both values of Λ_2 are surprisingly low, lower than expected even for single bonds. However, since a force constant represents the curvature in the potential energy function in the vicinity of the equilibrium configuration, it is reasonable to expect that when relatively stable configurations with only slight differences in geometry exist (the Kekulé forms in this case) the potential energy will change slowly, giving rise to an abnormally low force constant. This may also be the reason for the abnormally low force constants found for the central C–C bonds in diacetylene, for example.[4]

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[1] B. L. Crawford, Jr., and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

[2] R. D. Mair and D. F. Hornig, *ibid.*, **17**, 1236 (1949).

[3] N. Herzfeld, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 222 (1946).

[4] See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 323.

In terms of these force constants the distortion energy is

$$2E = \Lambda_1 S_1^2 + \Lambda_2 S_{14}^2$$

Since the necessary displacements are r_1, r_3, r_5 = −0.05 Å. and r_2, r_4, r_6 = 0.15 Å., the distortion energy is either 27.3 kcal./mole or 25.4 kcal./mole, depending on which value of Λ_2 is used. These values should be accurate to better than 5% since the displacements required are small, corresponding to the $n = 4$ vibrational level of S_{14} and a point between $n = 2$ and $n = 3$ for S_1. In the case of S_{14} it is known that the first overtone frequency deviates less than 0.2% from twice the frequency of the fundamental,[2] showing that the anharmonicity correction is very small.

Both of these values differ considerably from the value of the resonance energy (36 kcal./mole) derived from the heat of hydrogenation of cyclohexene.[5] It is of some interest to inquire wherein the difference may lie and to examine whether either value is suitable for comparison with the usual quantum mechanical calculation. The empirical resonance energy is customarily defined as the difference between the heat of formation of an idealized molecule consisting of *normal* single and double bonds and the heat of formation of the real molecule.[6] To be useful in the quantitative discussion of electronic structures, this definition should be taken to apply to the various species in their equilibrium states since the correction for zero point vibrational energies may constitute a considerable part of the total energy difference. In the case of benzene the idealized reference molecule has normal single and double bonds (and hence normal bond distances), and is non-strained and non-vibrating. The distorted state used in this work approximates this reference state in its dimensions but since it is still a real molecule some conjugation remains, in which case the mean value of the distortion energy, 26 kcal./mole, should be lower than the resonance energy and set a rigorous lower limit to the resonance energy.

The heats of hydrogenation, on the other hand, apply to the molecules at 355° K. and so they include both the thermal energy and the zero point vibrational energy of all of the molecules involved. In addition, there is some possibility that the reference molecule, cyclohexene, is strained.[7] It would be desirable to correct the data to 0° K. and the vibrationless state; unfortunately, sufficient data are not yet available to make this correction with any assurance. Reliable data are available on benzene[8]; reasonably reliable data are available on cyclohexane[9]; but the data on cyclohexene,[7] in particular the higher vibration frequencies and the estimated strain energy, are more uncertain. The portions of the heat content of the three molecules at 355° K. due to the sources mentioned are given in Table III on the basis of the references quoted.

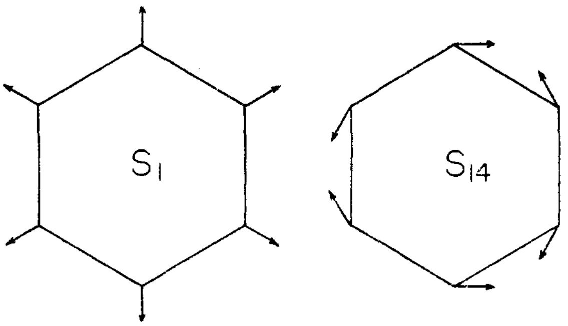

Fig. 1.—Symmetry coördinates involved in the distortion of benzene to a molecule with "normal" single and double bonds.

TABLE III

CORRECTION TO HEATS OF HYDROGENATION AT 355°K.

	$\sum_i \nu_i$ (cm.$^{-1}$)	Kcal. per mole		
		Zero point energy	$H-H_0$	Strain energy
Benzene	42,778	61.13	4.64	0
Cyclohexane	73,143	104.5	5.87	0
Cyclohexene	~61,150	~88.1	5.76	~1.6

It is apparent that the zero point energies are large and that the correction to the resonance energy involves differences between large, as yet unreliable, numbers. If the numbers in Table III are used literally, a net correction of −0.9 kcal./mole is obtained. It does not seem likely that the zero point vibrational energy of cyclohexene given in Table III is in error by as much as 1 kcal./mole or that the resulting correction is in error, from this source, by as much as 3 kcal./mole. The reliability of the strain energy estimate is more uncertain. Nevertheless, it is improbable that the total correction could be as great as 10 kcal./mole. In that case it is necessary to conclude that the resonance energy of the distorted configuration with Kekulé dimensions is still of the order of 10 kcal./mole and that reliable conclusions regarding bond type cannot be drawn from bond lengths alone.

It is clear, however, that neither of these values is suitable for comparison with the resonance energy as usually computed quantum mechanically, since in these calculations it is customary to use a reference state with non-interacting single and double bonds and a uniform C–C distance of 1.39 Å.[10,11] This reference state is certainly

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(5) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **58**, 146 (1936).

(6) See, for example, L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, Section 18 ff.

(7) C. W. Beckett, N. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948).

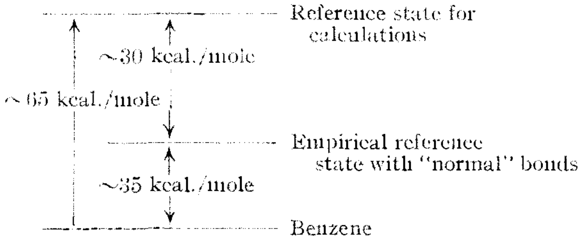
(8) API Project 44, National Bureau of Standards, "Selected Values of Properties of Hydrocarbons," Table 21u, November 30, 1945.

(9) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

(10) See, for example, H. Eyring, J. Walter and G. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 248 ff.

(11) J. van Dranen and J. A. A. Ketelaar, *J. Chem. Phys.*, **17**, 1338 (1949).

higher in energy than the empirical reference state containing normal single and double bonds. The magnitude of this difference may be estimated since it is obtained by stretching the double bonds and compressing the single bonds of a "normal" structure by 0.05 and 0.15 Å., respectively. If the normal single and double bond force constants are approximately 5.0×10^5 and 9.6×10^5 dynes/cm., we might guess that the energy difference between the reference states is of the order of 30 kcal./mole so that calculated resonance energies should be greater than empirical resonance energies by about this amount. This relation between the two reference states and the real molecule may be shown schematically as



A value of about 65 kcal./mole for the resonance energy calculated from the reference state with equal bond lengths reduces the discrepancy encountered in crude quantum mechanical calculations. In a zero order molecular orbital calculation the resonance energy and the energy of the first excited state are calculated in terms of one parameter. If the spectroscopic value for the energy of the first excited state is used to determine this parameter a resonance energy of 109 kcal./mole is obtained.[12] Ketelaar's first order treatment reduces this figure to 56 kcal./mole and his second order treatment cuts it to 40 kcal./mole. By comparison with the results obtained here, Ketelaar's final figure is definitely low.

In summary, it appears that (1) normal bond lengths in benzene are not sufficient to ensure normal structures and (2) that the empirical resonance energy of about 35 kcal./mole corresponds to a value of about 65 kcal./mole in the usual quantum mechanical calculation.

(12) This and the succeeding figures are taken from the table in ref. 11 by fitting the first electronic transition instead of the resonance energy.

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The Isolation of Mandelic Acid from Cedar Tar

BY CARROLL L. KEY AND ROY T. CLARK, JR.[1]

The cedar tar, which was used in this investigation, was the residue obtained from the fractional distillation of the oil from the wood of *Juniperus mexicana*. A crude oil was obtained from this tar by pyrolysis in an Engler distillation apparatus. The initial thermocouple reading inside the distillation flask during this process was 296° and the final reading was 380°. A 450-ml. fraction of oil which had a refractive index of 1.5014 at 25° and a boiling point range of 233–235° was obtained from the crude oil by fractionation in a vacuum fractionating still and systematic recombination of the cuts by refractive index and boiling point range through seven distillations. Several other fractions, which were obtained in this manner, were also investigated, but no mandelic acid was found.

Experimental

The saponification equivalent of the fraction of oil obtained by the above method indicated the presence of an ester which was probably the source of mandelic acid. This acid was isolated by refluxing the oil in 10% sodium hydroxide for three hours, acidifying the water layer, and extracting it with ethyl ether. The impure solid which remained when the ether evaporated was recrystallized from benzene. The melting point of this solid was found to be 118°; its molecular weight was 148 when determined by the Rast method; and its neutral equivalent was 153. The melting point was unchanged when a mixed melt of the unknown and pure DL-mandelic acid was made. The melting point of the anilide of the isolated acid was 152°, and the *p*-nitrobenzyl derivative melted at 124°. The foregoing data correspond to those listed for DL-mandelic acid.

Yield.—The total weight of the tar residue used to obtain the oil for this investigation was approximately 80,000 g., and the total weight of DL-mandelic acid recovered was approximately 4.5 g.; therefore, the yield of acid was less than 0.0001 of 1%.

(1) Abstracted from the thesis of Roy T. Clark, Jr., submitted in partial fulfillment of the requirement for the M. A. degree at the Southwest Texas State Teachers College, San Marcos, Texas.

DEPARTMENT OF CHEMISTRY
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RECEIVED JUNE 16, 1950

Heat Capacity of the Hydrazine–Water System[1]

BY E. W. HOUGH,[2] D. M. MASON AND B. H. SAGE

The isobaric heat capacities of hydrazine–water mixtures in the liquid phase at compositions from 0.5 to 1.0 weight fraction hydrazine were determined at bubble-point pressure in a stainless steel bomb calorimeter. Four sets of heat capacity measurements at different compositions were made in the temperature range from 40 to 90°. The density of the mixtures was determined for atmospheric pressure at 0 and 50°.

Experimental

A description of the equipment and techniques employed is available.[3,4,5] A stainless steel bomb calorimeter with a volume of approximately 1 liter was suspended by small wires within a vacuum jacket. An electrical heater was used to raise the temperature of the calorimeter and con-

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(1) This paper presents the results of one phase of research carried out for the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. W-04-200-ORD-1482 sponsored by the U. S. Army Ordnance Department.

(2) Stanolind Oil and Gas Company, Tulsa, Oklahoma.

(3) B. H. Sage and E. W. Hough, *Anal. Chem.*, **22**, 1304 (1950).

(4) W. P. White, "The Modern Calorimeter," (The Chemical Catalog Co.) Reinhold Publishing Corp., New York, N. Y., 1928.

(5) N. S. Osborne, H. F. Stimson and E. F. Fiock, *Nat. Bur. Standards, J. Res.*, **5**, 411 (1930).