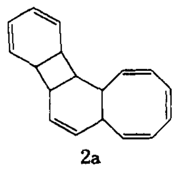
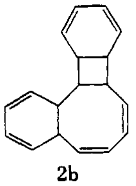
$CaCO_3$ to 1,2-benzo-1-cyclooctene (**6**), identified by direct comparison with an authentic sample.[7] The formation of benzene in this experiment was shown by glc of the dimethylformamide solution, the estimated yield being ~70%. Only trace amounts of other nonpolymeric products were obtained. The same substances **4** and **5** were formed when [18]annulene was boiled in diglyme (bp 161°) for 80 min.

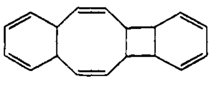
In order to discover intermediates in the conversion of **1** to **4** and **5**, the thermolysis of **1** in tetrahydrofuran-d_8 at various temperatures was monitored by nmr spectrometry. This showed that an intermediate was indeed formed after several hours at 90°, although its further transformation to **4** and **5** appeared to proceed at a rate comparable to its formation. In a preparative experiment, **1** in tetrahydrofuran was heated at 90° (sealed tube) for 9 hr, when the intermediate **2** could be isolated in ~5% yield as an apparently homogeneous colorless liquid [λ_{max} (cyclohexane) 268 nm (ϵ 5600)] by preparative layer chromatography on silica gel, together with ~75% of recovered **1**.[8]

The intermediate **2** was isomeric with [18]annulene, as shown by the mass spectrum at 25 eV (*m/e* 234).[9] Heating **2** in dimethylformamide at 130° for 11 hr led to its complete conversion to **4** and **5**, while photolysis in tetrahydrofuran-d_8 at −100° for 10 hr with four low-pressure Hg lamps gave **4** and [12]annulene (**7**),[10] identified by its typical nmr spectrum (τ 3.04 (s), 3.98 (s), ratio 1:1, at −115°), and its known transformations on heating above −40°.[10,11] Hydrogenation of **2** in benzene over Pt, followed by glc, gave two saturated hydrocarbons in a ratio of ~4:1, the mass spectra of which (*m/e* 246) showed them to be tetracyclic. This indicates that **2** is also tetracyclic, and this is in accord with the nmr spectrum ($CDCl_3$, 100 MHz) which showed multiplets at τ 3.85–4.55 (olefinic) and 6.40–7.95 (allylic) in a ratio of 2:1.

The three tetracyclic structures **2a**, **2b**, and **2c** are consistent with the above data, the ready thermal and photochemical elimination of benzene from such systems having precedent.[10,11] It has not been possible to distinguish between these structures, and the hydrogenation results suggest that **2** is probably a mixture of isomers.


2a


2b


2c

The thermolysis of **2** to **5** and its photolysis to **7** presumably involve *trans*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**3**)[10,11] as an intermediate, which must have the indicated stereochemistry since the corresponding cis isomer is known to give only benzene on thermolysis[10,11] (the thermolysis of **3** has not been studied previously; the photolysis of either **3** or the corresponding cis isomer at −100° is known to give [12]annulene[10]). The fusion between the eight- and the six-membered rings in **2** is therefore also trans.

Acknowledgments. We gratefully acknowledge the award of a Reichstein-Stipendium (to K. S.), and financial support from the Royal Society and the Fonds National Suisse de la Recherche Scientifique. We thank Dr. M. Vecchi, Hoffmann-La Roche, Basel, for glc–mass spectral measurements.

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Received July 21, 1972

The Additive Nature of Group Enthalpies of Transfer from Methanol to *N*,*N*-Dimethylformamide

Sir:

Enthalpies of transfer ($\Delta\Delta H_s$) of ions and nonelectrolytes from protonic solvents such as water or methanol to dipolar aprotic solvents such as dimethyl sulfoxide or dimethylformamide have recently been of interest to several investigators[1–5] in studying the role of solvents in certain anionic displacement reactions. These quantities ($\Delta\Delta H_s$) are involved in determining the enthalpy of transfer of the transition state ($\Delta\Delta H^t$) from one solvent to another through the expression

$$\Delta\Delta H^{t} = \Delta\Delta H_{s} + \Delta\Delta H^{\ddagger}$$

where $\Delta\Delta H^{\ddagger}$ is the difference in enthalpy of activation of the reaction in the two solvents.

Only a few enthalpies of transfer of nonelectrolytes have been reported[2–5] and no trends have been noted among the available data.[1a]

We have determined $\Delta\Delta H_s$ values from methanol (MeOH) to *N*,*N*-dimethylformamide (DMF) for a series of aromatic compounds and some of their nitro and chloro derivatives and wish to report evidence of a unique *additivity* of enthalpies of transfer for the phenyl, nitro, chloro, and acetyl substituents. Preliminary results indicate that an additive relationship also exists in aromatic compounds containing fluoro, bromo, iodo, and carbethoxy groups and in saturated compounds including alkanes, alkyl halides, and nitroalkanes. The aliphatic group values differ somewhat from the aromatic. Enthalpies of solution (ΔH_s) and enthalpies of transfer (both observed and calculated) are reported in Table I. A negative $\Delta\Delta H_s$ value indicates increased solvation in the transfer from MeOH to DMF.

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[7] Authentic **6** was obtained by catalytic hydrogenation of benzocyclooctatetraene, kindly provided by Mr. C. M. Bowes.

[8] Heating for more than 9 hr did not appreciably increase the yield of **2**, but resulted in larger amounts of **5** from which it was difficult to separate.

[9] The apparent molecular ion at 70 eV was at *m/e* 156, due to the ready elimination of benzene.

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Table I. Enthalpies of Solution in MeOH and DMF and Enthalpies of Transfer at 25° [a]

Compound	ΔH_s (MeOH), kcal/mol	ΔH_s (DMF), kcal/mol	$\Delta\Delta H_s$ (MeOH →DMF), kcal/mol	$\Delta\Delta H_s$ calcd, kcal/mol
Benzene	0.36	0.04	−0.3	
Biphenyl	4.3	3.7	−0.6	−0.6
o-Terphenyl	4.6	3.6	−1.0	−0.9
Naphthalene	4.5	3.9	−0.6	
Acetophenone	1.2	−0.1	−1.3	
Chlorobenzene	0.17	−0.25	−0.4	
o-Dichlorobenzene	0.34	−0.13	−0.5	−0.5
Nitrobenzene	1.0	−0.2	−1.2	
p-Nitrobiphenyl	5.6	4.2	−1.4	−1.4
p,p′-Dinitrobiphenyl	6.1	4.1	−2.0	−2.2
1-Nitronaphthalene	5.3	3.9	−1.4	−1.4
1-Chloronaphthalene	0.55	−0.19	−0.7	−0.7
o-Nitrochlorobenzene	4.7	3.6	−1.1	−1.2
m-Nitrochlorobenzene	5.6	4.4	−1.2	−1.2
p-Nitrochlorobenzene	4.2	3.0	−1.2	−1.2
2,4-Dinitrochlorobenzene	5.5	3.6	−1.9	−2.0
o-Nitroacetophenone	1.7	−0.6	−2.3	−2.1
m-Nitroacetophenone	6.6	4.5	−2.1	−2.1
p-Nitroacetophenone	6.4	4.2	−2.2	−2.1
p-Chloroacetophenone	1.13	−0.25	−1.4	−1.4

[a] All calorimetric values ±0.1 kcal/mol.

From the enthalpies of transfer of the neutral molecules the enthalpy of transfer for the various functional groups may be calculated in the following manner

$$\Delta\Delta H_s\,(\mathrm{NO_2}) = \Delta\Delta H_s\,(\text{nitrobenzene}) - \Delta\Delta H_s\,(\text{benzene})$$

$$\Delta\Delta H_s\,(\mathrm{Cl}) = \Delta\Delta H_s\,(\text{1-chloronaphthalene}) - \Delta\Delta H_s\,(\text{naphthalene})$$

$$\Delta\Delta H_s\,(\mathrm{COCH_3}) = \Delta\Delta H_s\,(\text{acetophenone}) - \Delta\Delta H_s\,(\text{benzene})$$

$$\Delta\Delta H_s\,(\mathrm{C_6H_5}) = \Delta\Delta H_s\,(\text{benzene}) = {}^1\!/_2\Delta\Delta H_s\,(\text{biphenyl}),\ \text{etc.}$$

The average values for the functional groups in kcal/g group wt are as follows: $\Delta\Delta H_s$ (NO_2) = −0.8, $\Delta\Delta H_s$ (Cl) = −0.1, $\Delta\Delta H_s$ ($COCH_3$) = −1.0, $\Delta\Delta H_s$ (C_6H_5) = −0.3.

Surprisingly, substituent $\Delta\Delta H_s$ values are not dependent on the overall molecular dipole moment. This is exemplified by the three nitrochlorobenzene isomers which have (within experimental error) the same enthalpy of transfer, but quite different dipole moments. The solvents appear to interact with each functional group individually without interference from ortho substituents, which results in additive values of $\Delta\Delta H_s$.

Group enthalpies of transfer will have a variety of applications when enough data are available, including the following. (1) Calculation of $\Delta\Delta H_s$ values of molecules without resorting to direct calorimetric measurements. Suppose, for example, one wished to calculate $\Delta\Delta H_s$ (2,4-dinitrochlorobenzene)

$$\begin{aligned}\Delta\Delta H_s^{\text{calcd}}\,(\text{2,4-dinitrochlorobenzene}) = {} & -1.6\ (\text{two nitro groups}) + \\ & -0.1\ (\text{chloro group}) + \\ & -0.3\ (\text{phenyl group}) = \\ & -2.0\ \text{kcal/mol}\end{aligned}$$

The observed value of $\Delta\Delta H_s$ (2,4-dinitrochlorobenzene) is −1.9 kcal/mol. Values obtained in this manner would be a convenience in transition-state $\Delta\Delta H$ studies, and would provide an approach to $\Delta\Delta H_s$ values of unstable molecules and molecules which rapidly solvolyze in the solvents of interest. (2) Studies of the interactions between individual functional groups and various types of solvents. (3) Observation of specific interactions between the functional group and the rest of the molecule which alter electron distribution and affect the additivity of $\Delta\Delta H_s$ (for example, a strong direct resonance interaction between $-NH_2$ and $-NO_2$ in *p*-nitroaniline).

We currently are investigating other functional groups using both aromatic and aliphatic models.

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant E-136) is gratefully acknowledged.

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Received September 18, 1972

Additions and Corrections

The Proton Magnetic Resonance Spectra of Olefins. V. 3-Chloro- and 3-Methoxypropenes [*J. Amer. Chem. Soc.*, 88, 2466 (1966)].

By Aksel A.B othner-By,* S. Castellano, S. J. Ebersole, and H. Günther, Mellon Institute, Pittsburgh, Pennsylvania 15213.

Linda Tomsyck and Professor R. Scott Pyron of Furman University have kindly pointed out to us that the values of ΔH, J^{g}, and J^{t} given for allyl chloride and allyl methyl ether are incorrect as a result of some computational error. We concur and confirm their findings that the best parameters are as follows (J in Hz and ΔH in cal). $CH_2{=}CHCH_2Cl$: J^{g}, 2.4; J^{t}, 11.6; J^{∞}, 5.5; ΔH, 958. $CH_2{=}CHCH_2OCH_3$: J^{g}, 2.3; J^{t}, 12.4; J^{∞}, 5.7; ΔH, −160.

Oxygen-17 Nuclear Magnetic Resonance Studies of Aqueous Nickel Ion [*J. Amer. Chem. Soc.*, 94, 3419 (1972)].

By James W. Neely and Robert E. Connick,* Department of Chemistry, University of California, and the Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California 94720.

The rounded off value of $\Delta S^{\neq}$ in Table III should be 9 eu. The kinetic parameters obtained in the least-squares fit were 13.88 kcal and 8.7 eu for $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively.

Neopentyl Displacement Reactions without Rearrangements [*J. Amer. Chem. Soc.*, 94, 4184 (1972)].

By Betty