

3,3-Dimethylbutan-1-ol³⁰ was prepared by hydroboration of 3,3-dimethylbut-1-ene, product bp 138–140° (lit.³¹ bp 141–143°).

3,3-Dimethylbutyl *p*-bromobenzenesulfonate (4)^{12a} was prepared from 3,3-dimethylbutan-1-ol and *p*-bromobenzenesulfonyl chloride. The nmr spectrum is consistent with that expected for this compound.

3,3-Dimethylbutyl(pyridine)bis(dimethylglyoximate)cobalt(III) was prepared by reaction of 4 with $\text{Co}(\text{dmgH})_2^-$ under a nitrogen atmosphere.³² The product was washed with ether to remove unreacted 4 and recrystallized from methanol by addition of an equal volume of a 1% solution of pyridine in water: pmr spectrum δ 0.75 (s, 9, C(CH₃)₃), 0.78 (m, 2, CH₂-2),³³ 1.63 (m, 2, CH₂-1),³⁰ 2.14 (s, 12, CH₃-dmgH), 7.20, 7.70, 8.58 (m, 5, pyridine); uv-visible spectrum in HClO₄ (aq), 453 nm (ϵ 1.47 \times 10³ M⁻¹ cm⁻¹), 387 (1.66 \times 10³).

Anal. Calcd for C₁₅H₃₃N₅O₅Co: Co, 13.0. Found: Co, 12.8.

3,3-Dimethylbutyl chloride³⁴ was prepared from *tert*-butyl chloride and ethylene using AlCl₃ catalyst, product bp 115–118° (lit.³⁴ bp 115–122°).

3,3-Dimethylbutylmercuric chloride was prepared by the reaction of mercuric chloride and 3,3-dimethylbutylmagnesium chloride in ether, product mp 133° (lit.³⁵ mp 133–133.5°).

***threo*-3,3-Dimethylbutan-1-ol-1,2-*d*₂ (1a)** was prepared by the methods of Whitesides, *et al.*,¹² product bp 138–140° (lit.³¹ 141–143°); deuterium-decoupled pmr spectrum (in CDCl₃)¹⁵ δ 0.92

(s, 9, C(CH₃)₃), 1.48 (d, J = 5.8 Hz, 1, CHD-2),³⁵ 3.66 (d, J = 5.8 Hz, 1, CHD-1),³⁵ 1.67 (s, 1, OH). This compound was converted to the *threo*-*p*-bromobenzenesulfonate (**1b**) on a 20 mmol scale analogous to the preparation of the undeuterated compound.

***erythro*-3,3-Dimethylbutyl-1,2-*d*₂-(pyridine)bis(dimethylglyoximate)cobalt(III) (2)** was prepared by adding 20 mmol of $\text{Co}(\text{dmgH})_2^-$ in methanol to a methanol solution of 20 mmol of **1b** over a period of 30 min. Excess NaBH₄ in the $\text{Co}(\text{dmgH})_2^-$ solution was destroyed with acetone to avoid reduction of **3** which might lead to racemization *via* eq 3; the isolated yield was 20%: deuterium-decoupled pmr spectrum (in CDCl₃)¹⁵ δ 0.75 (s, 9, C(CH₃)₃), 0.78 (d, 2, CHD-2, partially obscured by large singlet at 0.75), 1.63 (d, J = 13.2 Hz, 1, CHD-1).³⁷

***threo*-3,3-Dimethylbutyl-1,2-*d*₂-mercuric chloride (4)** was prepared by the reaction of **2** (0.56 mmol) in 250 ml of 0.20 *F* aqueous HClO₄ with Hg(ClO₄)₂ (0.56 ml of 1.0 *M* aqueous solution) at 75° with the exclusion of light. The reaction progress was monitored spectrophotometrically, and after 17 hr (80% completion) the solution was cooled to room temperature. Sodium chloride (1.12 mmol) was added to precipitate **3**, which was filtered and recrystallized from hot 95% ethanol, yield 30 mg of **3** (30%): Deuterium-decoupled pmr spectrum (in CDCl₃)¹⁵ δ 0.92 (s, 9, C(CH₃)₃), 1.58 (d, J = 5.3 Hz, 1, CHD-1),³⁸ 1.91 (d, J = 5.3 Hz, 1, CHD-2).³

Acknowledgment. We are grateful to Professor G. M. Whitesides for the synthetic procedures and to the University of Nebraska and Dr. D. Thoennes for the deuterium-decoupled nmr spectral measurements.

(36) The resonance at δ 3.67 also contains four smaller extraneous peaks thought to arise from the alcohol with partial deuterium scrambling; see Discussion Section. The doublet at δ 1.49 shows several smaller peaks also due to improperly deuterated molecules.

(37) The resonance at δ 1.63 also contains four smaller extraneous peaks from partial deuterium scrambling.¹⁵

(38) The resonance at δ 1.58 also contains four smaller extraneous peaks thought to arise from partial deuterium scrambling; see Discussion Section.

(30) G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963). We are grateful to Dr. R. C. Larock for suggesting this synthesis and for advice in carrying it out.

(31) R. C. Houston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(32) G. N. Schrauzer, *Inorg. Syn.*, **11**, 65 (1968).

(33) The multiplets at δ 0.78 and 1.70 ppm are the upfield and downfield parts of an A₂B₂ pattern; the pertinent nmr parameters are discussed in the body of the paper.

(34) A. Brandstrom, *Acta Chem. Scand.*, **13**, 611 (1959).

(35) F. C. Whitmore and H. Bernstein, *J. Amer. Chem. Soc.*, **60**, 2626 (1938).

Thermochemistry of Azoalkanes

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Abstract: The following enthalpies of formation (ΔH_f , kcal mol⁻¹) of five gaseous azoalkanes at 25° are calculated from the measured heats of combustion and vaporization: azoisopropane (**1**), 8.6; azo-*n*-propane (**2**), 12.4; azo-*tert*-butane (**3**), -10.4; 2,3-diazabicyclo[2.2.1]heptene-2 (**4**), 46.8; 1,4-dimethyl-2,3-diazabicyclo[2.2.2]octene-2 (**5**), 21.6. If the carbons α to the azo nitrogens are treated as aliphatic carbons, the revised thermochemical trans azo group contribution is 52.3 kcal mol⁻¹. Consideration of the difference between trans and cis azoalkanes allows calculation of upper limits on the ring strain energy of **4** and **5** of 11.3 and 6.4 kcal mol⁻¹, respectively. The values of ΔH_f are related to the activation energy of azoalkane thermolysis and are used to calculate that this process is less exothermic than previously estimated.

In recent years, there has been a great renewal² of interest in azoalkanes as sources of free radicals,⁴ for synthesis of strained ring systems,⁵ for study of orbital symmetry⁶ and spin correlation effects,⁷ and for

(1) On leave from David Lipscomb College, Nashville, Tenn.

(2) Early work on the gas-phase thermolysis of azoalkanes is cited in ref 3.

(3) R. Rebert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 1847 (1965).

(4) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 129.

(5) (a) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341 (1969); (b) R. Criegee, *Ber.*, **90**, 414 (1957); (c) G. L. Closs, L. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).

(6) W. Roth, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969); N. Rieber, J. Albers, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969).

testing unimolecular reaction theory.⁸ Moreover, the study of thermal⁹ and photochemical decomposition¹⁰ of azo compounds has become an active area of research.

Understanding the reactivity of azoalkanes would be greatly facilitated by a knowledge of their thermochem-

(7) P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970).

(8) S. S. Collier, D. H. Slater, and J. G. Calvert, *Photochem. Photobiol.*, **7**, 737 (1967); T. F. Thomas, C. I. Sutin, and C. Steel, *J. Amer. Chem. Soc.*, **89**, 5107 (1967).

(9) R. J. Crawford and K. Takagi, *J. Amer. Chem. Soc.*, **94**, 7406 (1972); J. Hinz, A. Oberlinner, and C. Rüchardt, *Tetrahedron Lett.*, 1975 (1973).

(10) For a recent review, see P. S. Engel and C. Steel, *Accounts Chem. Res.*, **8**, 275 (1973).

Table I. Summary of Typical Combustion Experiments for Compounds 1-5^a

Quantity	Compound				
	1	2	3	4	5
m' (compound), g ^b	0.34745	0.33910	0.33768	0.29878	0.29636
m'' (polyester), g	0.05982	0.05986	0.06133	0.06465	0.05904
m''' (oil), g				0.09448	0.09040
m'''' (cotton), g	0.00383	0.00427	0.00382	0.00400	0.00435
$\Delta t = t_j - t_i + \Delta t_{\text{corr}}$, °K	0.98940	0.96682	0.99968	1.07967	1.12127
e (calor)(Δt), cal	3517.67	3453.72	3554.21	3838.61	3986.52
ΔE ign, cal	0.74	0.60	0.74	0.74	0.74
ΔE (contents), cal ^c	-4.63	-4.58	-4.75	-5.05	-5.25
ΔE (corr to std states), cal ^d	1.22	1.08	1.05	1.35	1.23
ΔE (HNO ₃), cal	10.27	11.12	11.12	12.24	11.40
ΔE (polyester), cal	326.41	326.63	334.66	352.73	322.15
ΔE (oil), cal				1038.85	993.96
ΔE (cotton), cal	15.52	17.31	15.48	16.21	17.63
$m'\Delta E_c^\circ/M$ (compound), cal	-3168.13	-3101.55	-3195.91	-2421.53	-2644.70
$\Delta E_c^\circ/M$ (compound), cal g ⁻¹	-9118.23	-9146.42	-9464.31	-8104.73	-8923.94

^a The symbols and abbreviations used in this table are those of W. N. Hubbard, *et al.*, in "Experimental Thermochemistry," Vol. 1, F. D. Rossini, Ed., Interscience, New York, N. Y., 1956, pp 75-128. ^b Mass *in vacuo*. ^c $E'(\text{cont})(t_i - 25^\circ) + E'(\text{cont})(25^\circ - t_i + \Delta_{\text{corr}})$. ^d Items 81-85, 87-90, 93, and 94 from footnote a.

ical properties. For example, the relative stability of the *cis* and *trans* isomers and the magnitude of ring strain in cyclic azoalkanes are two questions of immediate interest. Thermochemical data on azo compounds are extremely meager; in fact, all calculated heats of formation are based on one set of experiments on azoisopropane (1) carried out in 1948.¹¹ This compound is not a typical azoalkane in at least one respect for it is now recognized^{12,13} that 1 exhibits anomalous activation parameters for thermal decomposition to nitrogen. It should also be mentioned that modern analytical techniques are more reliable than those employed 25 years ago and this alone provides ample justification for reexamining this early work. Combustion data have been reported for three other azo compounds but the values are not generally useful. *cis*- and *trans*-azobenzene¹⁴ are solids and their heats of sublimation are unmeasured; moreover, conjugation of the azo group with an aromatic ring introduces an unknown amount of resonance stabilization. Azoisobutyronitrile (AIBN), the widely used free radical initiator, has also been measured but detailed experimental data were not given.¹⁵ No value for its heat of sublimation has been reported, and in view of the thermal instability of this nonvolatile solid, such data will be difficult to obtain.

As the first task in the present investigation, the heat of formation of azoisopropane (1) was redetermined and found to differ by more than 10 kcal mol⁻¹ from that reported in the early work.¹¹ Our results for two other azoalkanes support the new value and allow calculation of the thermochemical group contribution of the azo group. This value and combustion data for two bicyclic azoalkanes were used to calculate the ring strain energy of these compounds, which turned out to be less than that of the analogous bicyclic olefins.

(11) G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).

(12) (a) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 136 (1966); (b) H. C. Ramsberger, *ibid.*, **50**, 714 (1928); (c) T. A. Wheatley, *Diss. Abstr.*, **21**, 3652 (1961); (d) S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962).

(13) G. Geiseler and J. Hoffmann, *Z. Phys. Chem. (Frankfurt am Main)*, **57**, 318 (1968).

(14) L. G. Cole and E. C. Gilbert, *J. Amer. Chem. Soc.*, **73**, 5423 (1951).

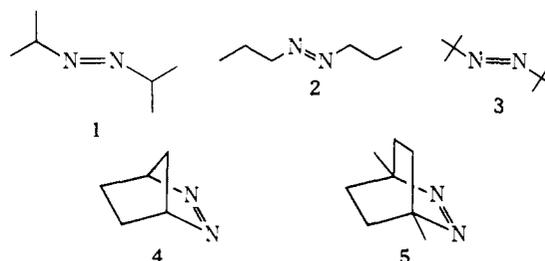
(15) W. S. McEwan and M. W. Rigg, *J. Amer. Chem. Soc.*, **73**, 4725 (1951).

Results

The compounds employed in this study are shown below. 1 was prepared¹⁶ from acetone hydrazone while 2 and 3 were synthesized by conversion of the appropriate amine to the sulfamide, followed by sodium hypochlorite oxidation to the azo compound.¹⁷



Compound 4 was prepared according to the published procedure¹⁸ and 5 was synthesized in a similar manner.¹⁹



At least five combustion runs were carried out on each compound with the results summarized in Tables I and II. Heats of vaporization were determined by measurement of the uv spectrum of the vapor above a

Table II. Summary of Combustion Energies for Individual Experiments

Quantity	Compound				
	1	2	3	4	5
$-\Delta E_c^\circ/M$, cal g ⁻¹	9116.77	9140.08	9473.55	8100.59	8926.39
	9116.29	9146.42	9464.31	8107.72	8935.04
	9109.02	9141.71	9461.81	8111.14	8924.93
	9118.23	9139.59	9462.44	8104.73	8923.94
	9119.57	9134.88	9456.79	8107.10	8931.39
Mean ^a	9115.97	9140.53	9463.78	8106.27	8928.33
	± 1.49	± 1.85	± 2.65	± 1.74	± 2.05

^a Uncertainties are standard deviations of mean.

(16) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(17) R. Ohme, H. Preuschhof, and H. U. Heyne, *Org. Syn.*, **52**, 11 (1972), and references cited therein.

(18) P. G. Gassman and K. T. Mansfield, *Org. Syn.*, **49**, 1 (1969).

(19) P. S. Engel, *J. Amer. Chem. Soc.*, **91**, 6903 (1969).

Table III. Thermochemical Data for Azoalkanes^a

Compd	ΔE_c°	ΔH_o°	ΔH_f (l or s)	ΔH_v^b	$\Delta H_f(g)$
1	-1041.00 ± 0.17	-1042.48 ± 0.17	-0.06	8.66	8.6
2	-1043.77 ± 0.21	-1045.25 ± 0.21	2.74	9.64	12.4
3	-1346.16 ± 0.39	-1348.23 ± 0.39	-19.01	8.64	-10.4
4	-779.27 ± 0.17	-779.86 ± 0.17	36.35	10.49	46.8
5	-1234.01 ± 0.28	-1235.49 ± 0.28	4.88	16.70	21.6

^a All values in kcal mol⁻¹. ^b Average of all determinations; see Table VI.

but, when placed into the mylar bag, it began evolving gas and was eventually converted to acetone plus several unknown products. Apparently air oxidation²³ was catalyzed by the mylar or some impurity and further work on this compound was abandoned.

A value for the azo group contribution to the heat of formation can be calculated from the relationship $\Delta H_f(g, \text{exptl}) = \Delta H_f^{\text{calcd}}(\text{alkyls}) + \Delta H_f(\text{azo})$ but a group value for each type of α -carbon must be assumed.²⁴ If azo nitrogen is taken to be the same as amino nitrogen, the values of $\Delta H_f(\text{azo})$ from compounds 1-3 show a spread of 3.7 kcal mol⁻¹, as shown in part (a) of Table IV. If, on the other hand, the azo group is

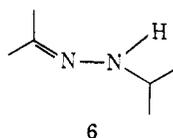
Table IV. Calculation of the Azo Group Contribution to ΔH_f

1	2	3
(a) Using Values for Carbon Bonded to Amino Nitrogen		
C-(H) ₃ (C) 4(-10.08)	C-(H) ₃ (C) 2(-10.08)	C-(H) ₃ (C) 6(-10.08)
C-(N)(C) ₂ (H) 2(-5.2)	C-(H) ₂ (C) ₂ 2(-4.95)	C-(N)(C) ₃ 2(-3.2)
	C-(N)(C)(H) ₂ 2(-6.6)	
$\Delta H_f^{\text{calcd}}(\text{isopropyls})$	$\Delta H_f^{\text{calcd}}(n\text{-Pr})$	$\Delta H_f^{\text{calcd}}(t\text{-Bu})$
= -50.72	= -43.26	= -66.88
$\Delta H_f(\text{azo}) = 59.3$	$\Delta H_f(\text{azo}) = 55.6$	$\Delta H_f(\text{azo}) = 56.5$
(b) Using Values for Carbon Bonded to Carbon		
C-(H) ₃ (C) 4(-10.08)	C-(H) ₃ (C) 2(-10.08)	C-(H) ₃ (C) 6(-10.08)
C-(C)(C) ₂ (H) 2(-1.90)	C-(H) ₂ (C) ₂ 2(-4.95)	C-(C)(C) ₃ 2(+0.5)
	C-(C)(C)(H) ₂ 2(-4.95)	
$\Delta H_f^{\text{calcd}}(\text{isopropyls})$	$\Delta H_f^{\text{calcd}}(n\text{-Pr})$	$\Delta H_f^{\text{calcd}}(t\text{-Bu})$
= -44.12	= -39.96	= -59.48
$\Delta H_f(\text{azo}) = 52.7$	$\Delta H_f(\text{azo}) = 52.3$	$\Delta H_f(\text{azo}) = 49.1$

liquid sample at a series of temperatures.²⁰ A summary of the thermochemical data for compounds 1-5 is shown in Table III.

Discussion

The ΔH_f for azoisopropane (1) determined by Coates and Sutton¹¹ was 19.5 kcal mol⁻¹, which is 10.9 kcal mol⁻¹ higher than our value. In seeking an explanation for this discrepancy, we considered the possibility that the samples used earlier contained tautomer 6,



which can be formed from the azoalkane by base catalysis.²¹ Unfortunately, the error is in the wrong direction because 6 is more stable than azoisopropane²² and its presence would lower the apparent ΔH_f . The samples of 1 used in this work did not contain 6, as shown readily by nmr and gas chromatography. Although no other explanation for the discrepancy comes to mind, our ΔH_f for 1 is reasonably consistent with data on compounds 2 and 3 as will be shown below.

It would be interesting to determine the ΔH_f of 6 by combustion calorimetry to supplement the equilibration studies.²² We prepared a sample of this tautomer

taken to be analogous to alkyl carbon as suggested in the clever analysis of Benson and O'Neal,²⁵ the spread is reduced to 3.6 kcal mol⁻¹ but azo-*tert*-butane stands apart from the other two compounds (*cf.* Table IV, part b). Inclusion of gauche interactions about the C-N bond only increases the discrepancy. Therefore either the experimental ΔH_f for azo-*tert*-butane is 3 kcal mol⁻¹ too low or tertiary α carbons really stabilize azoalkanes; that is, for electronic reasons the group contribution of tertiary α carbons should be more negative than the value used in Table IV. We presently favor the first idea because it corresponds to the usual direction of error in combustion experiments²⁶ and because it accounts for a discrepancy which arises when activation energies for azoalkane thermolysis are considered (see below). Although data for other acyclic tertiary azoalkanes would provide a firmer basis for this choice, their interpretation may be complicated by extra steric repulsion terms.

Based primarily on the results from 1 and 2, we suggest that the azo group contribution is 52.3 kcal mol⁻¹ when the α carbon is treated as ordinary alkyl carbon. The calculated ΔH_f of azomethane, the simplest azoalkane, then becomes 32.1 kcal mol⁻¹, which is much

(23) A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 3528 (1965), and references cited therein.

(24) The group contributions to ΔH_f are taken from ref 25.

(25) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21 (1970).

(26) An experimental combustion heat which is less negative than the true value can be rationalized by the presence of a more stable impurity or by incomplete combustion. The latter would reduce the precision of the measurements. In fact, the standard deviation for 3 is larger than that for the other compounds but it is too small to account for a 3 kcal mol⁻¹ error. The details of sample purification are given in the Experimental Section.

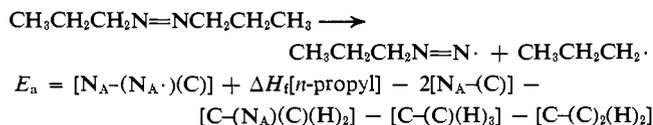
(20) This technique has been employed previously; see P. E. Fielding and A. G. Mackay, *Aust. J. Chem.*, 17, 1288 (1964); J. Jortner, E. G. Wilson, and S. A. Rice, *J. Amer. Chem. Soc.*, 85, 814 (1963); F. E. Stafford, *J. Chem. Educ.*, 40, 249 (1963).

(21) R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, 86, 745 (1964); H. L. Lochte, J. R. Bailey, and W. A. Noyes, *ibid.*, 44, 2556 (1922).

(22) B. V. Ioffe and V. S. Stopskij, *Tetrahedron Lett.*, 1333 (1968).

lower than the previous estimate of 43.8 kcal mol⁻¹.²⁵ An experimental determination of ΔH_f for azomethane would be of considerable help in confirming the azo group contribution to ΔH_f but the fact that it is an explosive gas is somewhat of an obstacle.

The relationship between thermochemistry and kinetics has been emphasized in several recent monographs.^{25, 27, 28} In view of the extensive literature on kinetics of azo compound thermolysis, it is of interest to relate the available data to the present heats of formation. Following the method of Benson and O'Neal,²⁵ we assume that gas-phase thermolysis of azo compounds proceeds by initial one bond scission.⁹ The activation energy (E_a) for this process can be expressed in terms of the thermochemical contribution of each carbon and nitrogen group, as illustrated below for azo-*n*-propane.²⁹ Another equation for each compound



expresses the experimental ΔH_f in terms of group contributions. For the sake of brevity, we introduce the following definitions: $[\text{N}_A-(\text{N}_A\cdot)(\text{C})] = a$; $[\text{N}_A(\text{C})] = b$; $[\text{C}-(\text{N}_A)(\text{C})_2(\text{H})] = c$; $[\text{C}-(\text{N}_A)(\text{C})_3] = d$; $[\text{C}-(\text{N}_A)(\text{C})(\text{H})_2] = e$. We can now write two equations for each compound, inserting the known²⁵ group contributions and heats of formation of radicals. Each pair of

Compound	E_a equation	ΔH_f equation
1	$a - 2b - c + 37.76 = E_a^1$	$2b + 2c - 40.32 = 8.6$
2	$a - 2b - e + 35.73 = E_a^2$	$2b + 2e - 30.06 = 12.4$
3	$a - 2b - d + 37.04 = E_a^3$	$2b + 2d - 60.48 = -10.4$

equations can be solved for $(a - b)$, which should be the same for each compound. Unfortunately, the activation energies for azoalkane thermolysis are not precisely known. Not only do similar compounds give unexpectedly different numbers, but the reported activation energy for any given one may vary between laboratories.³⁰ Using the preferred values of Benson²⁵ (47.5, 50.0, and 43.5 kcal mol⁻¹), we arrive at values of $(a - b)$ for compounds 1-3 of 34.2, 35.5, and 31.5, respectively. Gauche interaction terms enter into both equations in such a way as to cancel in the calculation of $(a - b)$. The discrepancy between azo-*tert*-butane and the other two compounds suggests that its experimental ΔH_f may be too low, as discussed above.

If $(a - b)$ is taken to be 34.0 kcal mol⁻¹, the fact that $\Delta H_f(\text{azo}) = 2b = 52.3$ kcal mol⁻¹ implies that the group contribution of a diazenyl radical is $a = 60.2$ kcal mol⁻¹. This figure can be used with the group additivity method to calculate ΔH_f for various diazenyl radicals and hence the exothermicity of nitrogen loss. The results, which are shown in Table V, are in accord with the expectation that the most exothermic reactions are the ones which produce the most stable products. The phenyldiazenyl radical is interesting because loss of

(27) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(28) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(29) The equation for E_a on p 31 of ref 25 contains a wrong sign for the term $[\text{C}-(\text{N}_A)(\text{H})_2(\text{C})_{3-2}]$.

(30) P. S. Engel, A. I. Dalton, and L. Shen, *J. Org. Chem.*, **39**, 384 (1974).

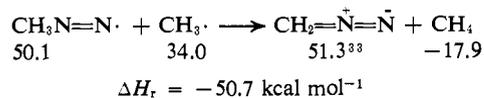
Table V. Exothermicity^a (ΔH_f) of the Reaction $\text{R}-\text{N}=\text{N}\cdot \rightarrow \text{R}\cdot + \text{N}_2$

R in $\text{R}-\text{N}=\text{N}-\text{R}$	E_a^b	$\Delta H_f(\text{R}-\text{N}=\text{N}-\text{R})^c$	$\Delta H_f(\text{R}-\text{N}=\text{N}\cdot)^d$	$\Delta H_f(\text{R}\cdot)^e$	ΔH_f
C_3H_5		(96.3) ^f	82.2 ^f	80.0	-2.2
CH_3	52.5	(32.1)	50.1	34.0	-16.1
<i>n</i> - C_3H_7	50.0	12.4	40.2	20.7	-19.5
<i>i</i> - C_3H_7	47.5	8.6	38.1	17.6	-20.5
<i>t</i> - C_4H_9	43.5	-10.4	30.5	6.8	-23.7
$\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)_2$	26.9 ^g	(45.0)	56.6	19 ^h	-37.6

^a All values are in kcal mol⁻¹. ^b Preferred values of Benson²⁵ for azoalkane thermolysis. ^c Values in parentheses are calculated by group additivity²⁴ according to Table IV, part b. ^d Calculated using $\Delta H_f(\text{diazenyl}) = 60.2$ kcal mol⁻¹. ^e Reference 25. ^f Assumes no resonance stabilization. ^g P. S. Engel and D. J. Bishop, *J. Amer. Chem. Soc.*, **94**, 2148 (1972). ^h D. K. Sen Sharma and J. L. Franklin, *ibid.*, **95**, 6562 (1973).

nitrogen is barely exothermic; in fact, if this radical possessed any resonance stabilization, the reaction would be endothermic. Strong evidence exists for the intermediacy of phenyldiazenyl radicals in homolysis of phenylazoalkanes.³¹

It is interesting to note that disproportionation of an alkyl-diazenyl radical pair is actually considerably more exothermic than loss of nitrogen. This reaction, which is illustrated below for azomethane, has been observed during decomposition of azocyclooctane³²



but could very well go undetected in most azoalkanes. Since the activation energy for disproportionation³⁴ may exceed that for loss of nitrogen and since both reactions are very fast, thermochemical factors may have little bearing on which one predominates.

As mentioned earlier, combustion data for only three azo compounds aside from azoisopropane have been reported. The missing link needed to compare those values with the present work is the heat of vaporization; nevertheless, it can be shown that AIBN fits in nicely. The reported¹⁵ ΔH_f of solid AIBN was 54.7 kcal mol⁻¹, a value which we confirmed in a single combustion experiment. The difference between this figure and the one calculated by group additivity (68.6 kcal mol⁻¹) is 13.9 kcal mol⁻¹, an entirely reasonable value for the heat of vaporization.

Examination of the available data for azobenzene leads to the surprising result that this compound possesses little resonance stabilization, in contrast to *trans*-stilbene³⁵ which has 7 kcal mol⁻¹. If one adds up the reported¹⁴ ΔH_f of solid *trans*-azobenzene (76.40 kcal mol⁻¹), its measured $\Delta H_f(1 \rightarrow g)$ (15.3 kcal mol⁻¹),³⁶ and an estimate of 4 kcal mol⁻¹ for the heat of fusion, $\Delta H_f(g)$ comes out 95.8 kcal mol⁻¹. Since this is nearly

(31) N. A. Porter and L. J. Marnett, *J. Amer. Chem. Soc.*, **95**, 4361 (1973).

(32) A. C. Cope and J. E. Engelhart, *J. Amer. Chem. Soc.*, **90**, 7092 (1968).

(33) A. H. Laufer and H. Okabe, *J. Amer. Chem. Soc.*, **93**, 4137 (1971).

(34) M. J. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973).

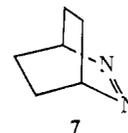
(35) R. B. Williams, *J. Amer. Chem. Soc.*, **64**, 1395 (1942).

(36) This figure is derived from data in D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

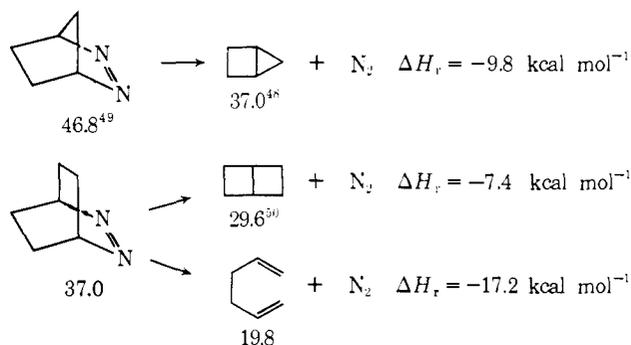
the same as the value in Table V, which was calculated on the assumption that azo nitrogen behaves like alkyl carbon, azobenzene appears to possess little extra stabilization. Before this conclusion is fully accepted, it would be necessary to determine the heat of sublimation directly and possibly to check the reported¹⁴ ΔH_f of the solid.

Heats of formation of the two bicyclic azo compounds **4** and **5** were determined with the aim of calculating their ring strain energy; however, the question immediately arises whether it is legitimate to compare cis with trans azo groups. Since cyclic *cis*-azoalkanes characteristically^{37,38} decompose to nitrogen more readily than their acyclic trans counterparts, there is some support for the idea that the *cis* azo group is of higher energy than *trans*. On the other hand, the ease of decomposition may reflect mostly the relative energy of the transition states. *cis*-Azoisopropane³⁹ was prepared in an attempt to shed some light on this matter but on account of its nasty tendency to tautomerize, it never could be obtained in the quantity and purity needed for combustion calorimetry.⁴⁰ Several runs on our purest material gave a heat of combustion approximately equal to that of the *trans* isomer but its heat of vaporization was 1.85 kcal mol⁻¹ higher than that of *trans*. We can therefore state that the *cis* azo group contribution is at least 54.2 kcal mol⁻¹. From the definition ΔH (strain) = $\Delta H_f(\text{exptl}) - \Delta H_f(\text{calcd})$, we can compute the maximum strain energies of **4** and **5** to be 11.3 and 6.4 kcal mol⁻¹, respectively. Comparison with the analogous hydrocarbons is interesting. The most recent determination⁴¹ of the strain energy of norbornene gave a value of 17.6 kcal mol⁻¹ but previous reports indicated higher values. Thus the azo compound **4** is at least 6.3 kcal mol⁻¹ less strained than norbornene. Similarly, the strain energy of bicyclo[2.2.2]octene⁴² is 10.5 kcal mol⁻¹, so that the azo compound is less strained by at least 4.1 kcal mol⁻¹. A possible explanation³⁸ for this difference would invoke relief of unfavorable interaction between the *n* orbitals on nitrogen when the C—N=N angle is decreased. Alternately, the smaller natural C—N=N bond angle (112–116°)^{43,44} relative to C=C=C may be the reason why an azo group is more easily incorporated into a strained ring.

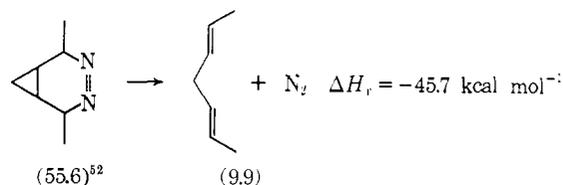
The activation energy for thermal loss of nitrogen from **4**⁴⁵ is 37.1 kcal mol⁻¹ while that for **7**^{12d} is 44.6 kcal mol⁻¹. Although the kinetics have not been studied for **5**, we would guess that its transition state is of slightly lower energy than that of **7**, on account of the tertiary α carbons. Thus the difference in ground-



state strain between **4** and **5** (4.9 kcal mol⁻¹) may well account for all of the difference in E_a . From the heat of formation of **4** and **5**, we may calculate enthalpies for decomposition of **4** and **7**. In fact, the reactions are less exothermic than previously estimated.^{46,47}



Since the total energy available to the products during photolysis of azo compounds is augmented by the energy of the light, we may inquire into the possibility of producing electronically excited nitrogen ($E = 142$ kcal mol⁻¹). Assuming that 366-nm (78 kcal mol⁻¹) irradiation is used, a reaction enthalpy of -64 kcal mol⁻¹ will be required. The above compounds fall far short of this figure and even the example below⁵¹ is not sufficiently exothermic to produce excited nitrogen.



Experimental Section

(1) **Preparation and Purification of Compounds.** Azoisopropane (**1**) was obtained in three steps from acetone according to the well-established literature procedure.¹⁶ Spinning band distillation afforded material boiling constantly at 88.5°. Its nmr spectrum agreed with that reported in the literature³⁹ and vpc on a 0.25-in. 10% SF-96 column at 110° showed only one symmetrical peak. Azo-*n*-propane (**2**) was prepared by oxidation of the sulfamide by the elegant procedure of Ohme, Preuschhof, and Heyne.¹⁷ Attempted distillation at atmosphere pressure resulted in considerable decomposition but no difficulties were encountered during vacuum distillation. The material boiled constantly at 54° (87 mm) and showed no impurities by vpc. Azo-*n*-propane gave the following nmr spectrum δ 0.93 (t), 1.70 (distorted sextet), and 3.66 (t). Azo-*tert*-butane (**3**) was also synthesized *via* the sulfamide¹⁷

(46) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21, 337-338 (1970).

(47) T. F. Thomas and C. Steel, *J. Amer. Chem. Soc.*, **87**, 5290 (1965).

(48) S. Chang, D. McNally, S. S. Tehrani, M. J. Hickey, and R. H. Bold, *J. Amer. Chem. Soc.*, **92**, 3109 (1970).

(49) Calculated from the data for compound **5**.

(50) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser. Nat. Bur. Stand.*, No. 21, 328 (1970). Formation of this product occurs on photolysis; see W. D. K. Clark and C. Steel, *J. Amer. Chem. Soc.* **93**, 6347 (1971).

(51) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **92**, 1086 (1970).

(52) Calculated using the ring strain energy of **5** and $\Delta H_f(\text{cis azo}) = 54.2$ kcal mol⁻¹.

(37) K. R. Kopecky and S. Evani, *Can. J. Chem.*, **47**, 4041 (1969); D. Lim, *Collect. Czech. Chem. Commun.*, **33**, 1122 (1968), structure II is incorrect.

(38) T. Mill and R. S. Stringham, *Tetrahedron Lett.*, 1853 (1969).

(39) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 1220 (1969).

(40) Solution calorimetry offers an appealing alternative for measuring ΔH_f of *cis*-azoisopropane.

(41) H. K. Hall, C. D. Smith, and J. H. Baldt, *J. Amer. Chem. Soc.*, **95**, 3197 (1973).

(42) Calculated using the group values from ref 25 and the experimental determination of S. S. Wong and E. F. Westrum, *J. Amer. Chem. Soc.*, **93**, 5317 (1971).

(43) C. H. Chang, R. F. Porter and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 5313 (1970).

(44) D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, **92**, 4586 (1970).

(45) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

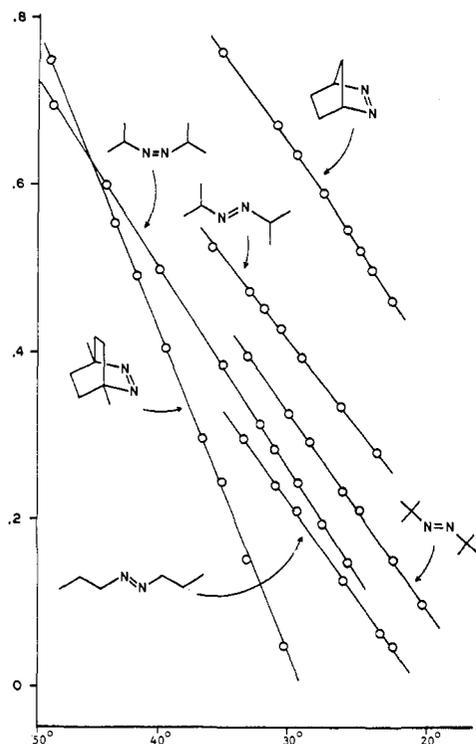


Figure 1. Clausius-Clayperon plot for azoalkanes. The horizontal axis is linear in reciprocal temperature while the vertical axis is $\log P'$ calculated from eq 1 plus an arbitrary additive constant to avoid excessive overlapping of lines.

and was spinning band distilled (bp 109°). Its purity was checked by vpc and nmr (δ 1.16, s). Diazabicycloheptene (**4**) was prepared by the standard sequence from cyclopentadiene and ethylazodicarboxylate.¹⁸ After recrystallization from pentane, it was sublimed three times, mp 98–100°. The synthesis of **5** was carried out by catalytic hydrogenation and hydrolysis^{5a} of the adduct of 1,4-dimethyl-1,3-cyclohexadiene⁵³ and 4-phenyl-1,2,4-triazoline-3,5-dione.⁵⁴ This method was a considerable improvement over that employed previously.¹⁹ **5** was liberated from its cuprous chloride complex by treatment with aqueous sodium hydroxide¹⁸ and purified by subliming twice: mp 70.5–71.5°; nmr δ 1.29 (symmetrical broad quartet) and 2.12 (sharp singlet).

(2) **Calorimetry Equipment.** The calorimeter used was of the Argonne National Laboratories Design CT-3986. Although this calorimeter is designed for rotating bomb operation, this feature was not used in the experiments described here. The bomb used was a Parr Model 1105. A platinum crucible weighing approximately 16.08 g was used to hold the samples.

The temperature of the calorimeter jacket was maintained at $26.500 \pm 0.001^\circ$ by a Bayley Precision Temperature Controller. The combustion experiments were carried out in such a way that the burning process began at $25.000 \pm 0.005^\circ$. The temperature of the water in the calorimeter bucket and the jacket was measured with a Hewlett-Packard Dymec quartz thermometer Model 2801A connected to a Model 2850D probe. For most of the compounds studied the digital output of this thermometer was converted by means of an interface into a form usable by a Model ASR 33 Teletype which provided a permanent temperature-time record of the combustion experiment. The ignition energy was supplied by a pulse-counter circuit driven by the quartz thermometer which could be preset to charge and fire at the proper time during the combustion experiment.

Oxygen from a high pressure cylinder was purified by passing through a 600° column of copper oxide and then through absorption tubes of Ascarite and magnesium perchlorate.

(3) **Calibration of the Calorimeter.** Two series of calibration experiments were made using National Bureau of Standards calorimetric standard sample 39i benzoic acid weighed in the form

(53) K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **608**, 195 (1957).

(54) R. C. Cookson and S. K. Gupte, *Org. Syn.*, **51**, 121 (1971).

of pellets and ignited by means of a cotton thread. The energy of combustion of this benzoic acid using the bomb conditions described in the certificate of calibration was $\Delta E_o = -6817.48 \pm 0.07 \text{ cal g}^{-1}$.⁵⁵ The first calibration series yielded a value for the energy equivalent of the calorimeter, ϵ (calor) = $3555.35 \pm 0.57 \text{ cal deg}^{-1}$. This value was used in calculating $\Delta E/M$ for compounds **1**, **3**, **4**, and **5**. Several minor changes were later made in the calorimeter system which required a new calibration. This new value of the energy equivalent was ϵ (calor) = $3572.25 \pm 0.50 \text{ cal deg}^{-1}$ and was used for compound **2**.

The combustion experiments for the calibration and the azo compounds were corrected to standard states using the usual techniques⁵⁶ of computation. A computer program was written in Fortran IV to handle these computations. The temperature-time data were also evaluated by computer using standard methods of calculation⁵⁷ to yield a best value of ΔT . The amount of benzoic acid burned was the mass corrected *in vacuo*.

(4) **Combustion of the Azo Compounds.** Each of the compounds was burned in polyester bags. The energy of combustion of this polyester was $\Delta E_o/M = -5457.4 \text{ cal g}^{-1}$.⁵⁸ Compounds **4** and **5** were burned with a sample of mineral oil as a combustion aid. The energy of combustion of this mineral oil was determined to be $\Delta E_o/M = -10,985.07 \pm 0.81 \text{ cal g}^{-1}$. A cotton thread, $\Delta E_o/M = -4050 \text{ cal g}^{-1}$, was tied about the polyester bag and was ignited by a platinum wire tied between two electrodes in the bomb.

The nitric acid formed in the combustion process was titrated ($\pm 0.002 \text{ ml}$) with 0.1 *N* NaOH and the heat evolved from the formation of 0.1 *N* HNO₃ was taken to be 13.81 kcal mol⁻¹.⁵⁹ The acid contents from several combustion experiments on each compound were tested for the presence of HNO₂ using techniques sensitive to 10⁻⁴ mol. No thermochemically significant amounts were ever found.

(5) **Calculation of the Heats of Combustion.** All masses of the substances in the bomb were connected *in vacuo*. The heat capacities of the azo compounds were estimated using Kopp's law. The quantity $(\delta E/\delta T)_T$ was estimated for each compound and was taken to be approximately $-0.003 \text{ cal g}^{-1} \text{ atm}^{-1}$.

(6) **Enthalpies of Vaporization.** The azo compounds employed in this study have the unique property of being volatile materials which absorb at long wavelength (>300 nm) in the uv region. This suggested that their relative vapor pressure could be determined by measuring the absorbance of the vapor above a quantity of liquid. The heat of vaporization would then be calculated from the variation of absorbance with temperature. Combination of the ideal gas law with Beer's law leads to the equation

$$a = \epsilon l P' / 62.4 T \quad (1)$$

where a = absorbance, ϵ = extinction coefficient, l = path length in cm, T = absolute temperature, and P' = pressure in millimeters. Assuming that an absorbance of 0.03 can be measured accurately, that a 10-cm cell is used, and that T is 298°K, we find that the product $\epsilon P'$ must be at least 55 for the method to be practical. For the *trans*-azoalkanes, ϵ is about 14 so a vapor pressure of about 4 mm is required. This condition is very easily met in compounds **1–3** but **4** and **5** are less volatile than the others. Fortunately the value of ϵ is about ten times higher for *cis*-azoalkanes than *trans* so that all of the compounds have sufficient absorbance.

One advantage of the optical method is that materials with low vapor pressure can be studied without precise knowledge of their extinction coefficients. In the plot of $\log P'$ vs. T^{-1} , the value of ϵ determines only the vertical position of the line and not its slope, which is the quantity of interest. It is apparent from Figure 1 that data for most of the azo compounds lie on a straight line. The slight downward curvature in some cases is in accord with the expected decrease of ΔH_v at higher temperature; however, the curvature is too severe in compound **4** to be rationalized on this basis. One possible explanation derives from the extraordinary uv spectrum of **4**, which, in contrast to the other compounds, exhibits a great number of exceedingly sharp lines. Pressure broadening of the lines could account for their abnormally small height at the

(55) In this paper 1 cal = 4.184 J.

(56) W. N. Hubbard, *et al.*, in "Experimental Thermochemistry," Vol. 1, F. D. Rossini, Ed., Interscience, New York, N. Y., 1956, pp 75–128.

(57) J. Coops, *et al.*, in ref 56, pp 27–58.

(58) This value is for the temperature and humidity conditions of this laboratory.

(59) E. J. Prosen in ref 56, pp 129–148.

Table VI. Vaporization Heats of Azo Compounds, kcal mol⁻¹

Compound	ΔH_v (uv)	ΔH_v (other)
Azoisopropane (1)	8.63	8.33, ^a 9.00 ^b
Azo- <i>n</i> -propane (2)	9.45	9.82 ^a
Azo- <i>tert</i> -butane (3)	9.47	7.81 ^b
2,3-Diazabicyclo[2.2.1]heptene-2 (4)	10.5	10.0, ^b 10.6 ^c
1,4-Dimethyl-2,3-diazabicyclo-[2.2.2]octene-2 (5)	16.70	

^a Reference 13. ^b Determined in this laboratory using a modified isoteniscope. ^c C. Steel, unpublished result.

higher temperatures. An alternative explanation would say that the apparent curve is actually two straight lines and that a solid phase transition occurs at their intersection with a ΔH of about 1.3 kcal mol⁻¹. Despite the problem with 4, the average value of ΔH_v

does not differ greatly from the other determinations as shown in Table VI.

The heat of vaporization apparatus consisted of a quartz cell connected *via* a graded seal and sealing constriction to a 10/30 joint. After the compound was degassed and sealed in the cell under high vacuum, the cell was placed into a thermostated silicone oil bath fitted with quartz end windows. The whole assembly, which had a volume of about 200 ml, was placed in the cell compartment of a Cary 17 spectrometer. The temperature was regulated by a Bayley Controller and monitored by a thermistor and wheatstone bridge. Temperature control was better than 0.03°.

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Molecular Structure of Ion Pairs from Electric Dipole Moments. I. Potassium *p*-Toluenesulfonate and Lithium Chloride in Octanoic Acid¹

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Abstract: Measurements of the permittivity of dilute solutions in octanoic acid at 25° led to the following electric dipole moments: for LiCl ion pairs, μ 6.78 D (as compared with 7.12 D in the gas phase); for potassium *p*-toluenesulfonate (KTs) ion pairs, μ 4.8 D. It was found that $2\text{LiCl} \rightleftharpoons (\text{LiCl})_2$; $K = 183 \pm 20$; μ for $(\text{LiCl})_2 \sim 0.0$. Analysis of the dipole moment of KTs establishes a symmetrical structure in which the K⁺ ion sits on, or very near, the symmetry axis of the Ts⁻ ion, adjacent to the plane defined by the oxygen atoms. In carrying out this analysis, the noncentric tosylate ion is treated as a point dipole superposed on a point charge and the position of this *electric center* is precisely defined. The polarizability is divided into two parts which are treated as point polarizabilities, one of which is located at the electric center. The K-O distance is evaluated as 3.15 Å.

In spite of the importance of ion pairing in the chemistry of electrolytic solutions,²⁻⁴ relatively little is known about the molecular structure of the ion pairs. For ion pairs involving radical anions, it is clear from esr spectra that the cation attaches itself to the anion at specific sites.^{4,5} For ion pairs formed from ions with stable electron configurations, it is often assumed that the binding takes place so as to bring the centers of ionic charge to a closest approach.^{2,3,6} For ions such as Li⁺, Cl⁻, (CH₃)₄N⁺, or ClO₄⁻, which have centric charge distributions, the center of ionic charge is well defined by symmetry. However, for unsymmetrical ions such as anilinium⁺ or *p*-toluenesulfonate⁻ (Ts⁻), the position of the center of charge is open to some ambiguity. One would like to choose the position so that the electric field of the ion is that of an ionic charge

superposed on a dipole of predictable magnitude and direction. (Electric moments higher than the dipole moment will be neglected.) If such a choice were objectively possible, then the measured dipole vector for the ion pair, in combination with the dipole vectors of the constituent ions, would enable us to find the radius vector joining the centers of ionic charge and thus to deduce the molecular structure of the ion pair.

LiCl in Octanoic Acid. Specifically, we have measured electric dipole moments for LiCl and KTs in octanoic acid. The latter solvent was chosen because of its relatively good solvent action for electrolytes, coupled with a low dielectric permittivity (ϵ 2.48 at 25°). LiCl was chosen to provide a control experiment. The dipole moment of LiCl in the gas phase is 7.12 D.^{7,8} Our experimental result in octanoic acid, calculated according to Onsager's theory,^{9,10} is 6.78 D. The reasonable agreement between the two values indicates that in spite of the hydrogen-bonded solvent structure, accurate dipole moments for ion pairs can

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