Table I. MNDO Calculated Heat of Formation (kcal/mol) for Anions, σ and π Radicals

compd	anion	σ	π	E (π-σ)
NH_2	47.32	76.60	36.51	−40.11
HN_2 (MINDO/3)	56.44	53.36	29.06	−24.30
3a	−44.28	18.53	3.38	−15.15
3b	−52.21	10.37	−4.84	−13.17
3c	−217.79	−124.11	−140.74	−16.63
4a	−97.74	−19.96	−22.67	−2.71
5a	−101.72	−35.16	−30.83	4.33
5b		−9.36	−9.42	0.6
5b (nonplanar)		−13.00	−9.23	−3.77
5c	−110.12	−44.01	−40.15	3.85
5d	−280.54	−179.58	−177.75	1.83
6	−113.07	−23.71	−38.26	−14.55
pyrrole	14.27	97.13	55.85	−41.28

Table II. MNDO Calculated Geometries for Anions and σ and π Radicals

		N-H	C-O	C-N	OCO	NCO	CNC	HNC
HN_2	anion	0.98						
	σ	0.97						
	π	1.00						
NH_2	MINDO/3							
	anion	1.07						
	σ	0.98						
	π	1.04						
3a	anion	1.01	1.26	1.33		128.7		112.4
	σ	1.01	1.33	1.29		125.8		115.9
	π	1.01	1.23	1.41		122.9		113.1
3b	anion	1.01	1.27	1.34		126.16		112.0
	σ	1.01	1.33	1.30		122.90		115.4
	π	1.00	1.24	1.42		120.61		112.7
3c	anion	1.00	1.24	1.32				114.6
	σ	1.00	1.33	1.29				115.6
	π	1.00	1.23	1.40				113.4
4a	anion	1.13	1.24	1.37		122.5	119.0	
	σ	1.11	1.22	1.38		122.1	151.4	
	π	1.11	1.22	1.43		120.2	108.4	
			1.28					
5a	anion		1.26		125.6			
			1.26					
	σ		1.23		120.3			
			1.33					
	π		1.28		118.4			
			1.28					
5b	σ		1.23		127.5			
	(planar)		1.34					
	π		1.26		115.3			
	(planar)							
	σ		1.23		118.7			
			1.33					
	π		1.26		117.1			
			1.26					
5c	anion		1.26		123.6			
			1.26					
	σ		1.34		117.8			
			1.23					
	π		1.29		117.4			
			1.29					
5d	anion		1.24		130.9			
			1.24					
	σ		1.33		124.5			
			1.22					
	π		1.28		120.4			
6	anion	1.11	1.24	1.34		124.6	109.4	
	σ	1.11	1.21	1.39		109.4	120.0	
	π	1.11	1.22	1.43		120.2	108.4	
pyrrole	anion			1.37				105.5
	σ			1.37				117.0
	π			1.37				105.6

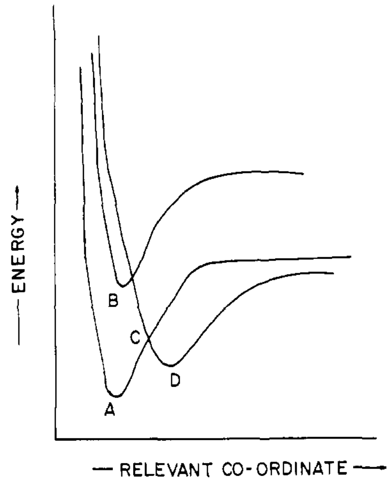

Figure 1. A → B represents a normal σ → π* transition. If the transition energy is low and the geometry of the "excited" structure D differs sufficiently from that of A, D may represent a local minimum on the *ground-state* surface, separated from A by a barrier (C).

in σ acyloxy radicals to be unequal, like those in the carboxylic acids from which they are derived (cf. Table II). The conclusion that **5b** is a σ radical with equal CO bond lengths is therefore difficult to accept. Our calculations seem to provide a possible solution of this problem. If the difference in energy between the σ and π forms of **5b** is indeed negligible, interconversion of the two mirror-image forms of the σ radical via the σ radical may be fast on the ESR time scale, leading to time-averaged equivalence of the oxygen atoms.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out with the Dual Cyber 170/150 computer at the University of Texas Computation Center.

Registry No. **3a** anion, 67131-48-0; **3a** radical, 14753-22-1; **3b** anion, 63285-19-8; **3b** radical, 7065-76-1; **3c** anion, 81583-99-5; **3c** radical, 81602-55-3; **4a** anion, 81584-00-1; **4a** radical, 75090-36-7; **5a** anion, 71-47-6; **5a** radical, 16499-21-1; **5b** anion, 766-76-7; **5b** radical, 1854-28-0; **5c** anion, 71-50-1; **5c** radical, 13799-69-4; **5d** anion, 14477-72-6; **5d** radical, 16040-26-9; **6** anion, 28627-67-0; **6** radical, 24344-83-0; NH_2 anion, 17655-31-1; NH_2 radical, 13770-40-6; HN_2 anion, 71004-29-0; HN_2 radical, 36882-13-0; pyrrole anion, 23303-09-5; pyrrole radical, 81584-01-2.

Tritium Migration in Tritiated Anisole

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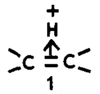
1,2 Wagner–Meerwein hydrogen shifts take place with extreme ease, due to the stability of the intermediate π complex[1] (**1**).



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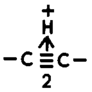

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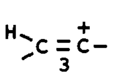

3

Recent MINDO/3[2] and "state-of-the-art" ab initio[3] calculations and experimental studies[4] have indeed indicated that the π com-

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(1) (a) Dewar, M. J. S. *J. Chem. Soc.* **1946**, 406; Bull. *Soc. Chim. Fr.* **1951**, *18*, c 71; "The Electronic Theory of Organic Chemistry"; Clarendon Press; Oxford, 1949. (b) Dewar, M. J. S.; Marchand, A. P. *Ann. Rev. Phys. Chem.* **1965**, *16*, 321.

(2) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 7432.

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(4) Dannenberg, J. P.; Goldberg, B. P.; Barton, J. K.; Dill K.; Weinwurzel, D. H.; Longas, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 7764.

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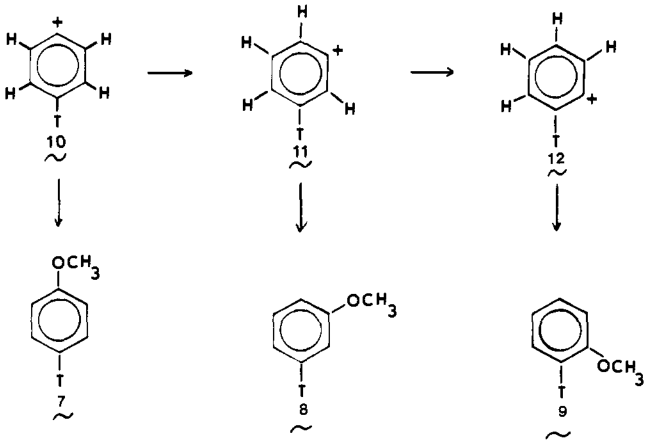
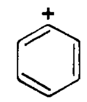
Scheme I



plexes from ethylene or 1,2-dialkylethylenes are more stable than the isomeric classical carbonium ions. Calculations[2,3] indicate that the same is true of the π complex **2**, derived from acetylene and isomeric with vinyl cation **3**. It is interesting to note that this is an area where MINDO/3 performs exceptionally well, better than any but the most refined ab initio treatments.[5]

The possible occurrence of similar 1,2 hydrogen shifts in aryl cations has been a topic of continuing interest for many years. The intermediate in this case is a protonated aryne, e.g., **4** in the case of phenyl cation (**5**). However, ab initio Roothaan–Hall calculations[10] using the STO-3G basis set and MINDO/3[11] both predict large barriers to migration (STO-3G, 77 kcal/mol; MINDO/3, 44 kcal/mol). For reasons indicated above, the MINDO/3 value is almost certainly nearer the truth, yet even it is large enough to make such a rearrangement very unlikely. The instability of **4** is of course due to the weakness of the three-center bond in it, due to the poor overlap of the AOs involved.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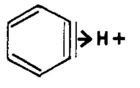
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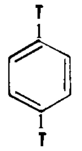
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Recently, however, two experimental studies[12,13] have been reported of reactions involving the phenyl cation (**5**) as an intermediate where the results obtained are most easily explained in terms of 1,2 hydrogen shifts in the intermediate ion (**5**). Our purpose here is to present an alternative interpretation, supported by MINDO/3 calculations, that avoids the implied conclusion that the barrier to hydrogen migration in **5** is in fact small.

Speranza[12] studied the reactions of tritiated **5**, produced by radioactive decay of one tritium nucleus in *p*-ditritiobenzene (**6**), with methanol, both in solution and in the gas phase. In solution the sole product was the (expected) *p*-tritioanisole (**7**) but in the gas phase the meta (**8**) and ortho (**9**) isomers were also formed, in the ratios **7**/**8**/**9** = 75.6:16.7:7.7.

Scheme II

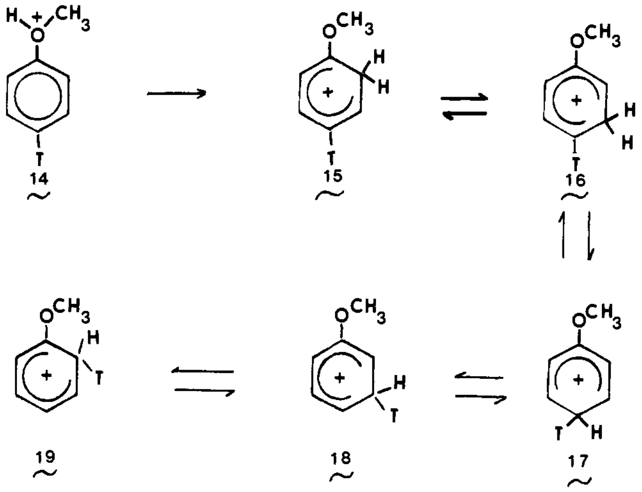


Table I. Calculated Heats of Formation and Proton Affinities

compd	protonated species	$\Delta H_f°$, kcal/mol	PA, kcal/mol
7[a]	**20**	150	197
7	**21**	137	209
7	**22**	158	183
7	**23**	134	213
MeOH	$MeOH_2^+$		181[b]
C_6H_6	$C_6H_7^+$		183[c]

[a] Calculated value is for nontritiated anisole. [b] Value from ref 14. [c] Value from ref 15.

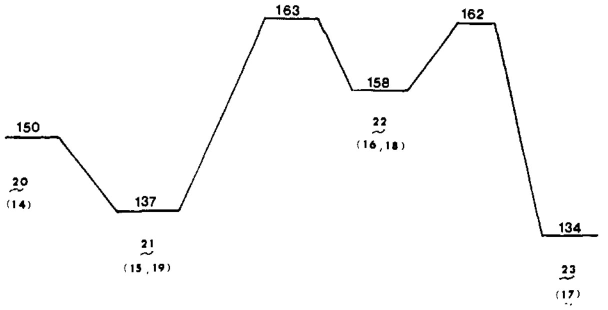
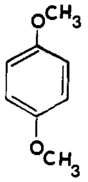


Figure 1. MINDO/3 energy profile for hydrogen (tritium) scrambling in protonated anisole (energies in kcal/mol).

As indicated above, Speranza interpreted his results in terms of 1,2 hydrogen shifts in the tritiated phenyl cation as shown in Scheme I. Since *p*-dimethoxybenzene (**13**) remained unchanged under the reaction conditions, migration of methoxyl could not have been responsible.


13

There is, however, another possibility that Speranza did not consider, i.e., rearrangements by hydrogen migration in the protonated anisole formed from methanol and **10**. This mechanism is shown in Scheme II. Here the intermediate π complexes are formed by attachment of the proton to the normal π MOs of anisole and so should be stable. Indeed, migrations of hydrogen

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(5) For example, MINDO/3[6] agrees with the very refined calculations by Koehler and Lischka in predicting the edge-protonated form of cyclopropane[3a] to be the most stable, also giving an excellent estimate of its energy relative to *i*-Pr. Other examples are calculations for the $C_7H_7^+/C_7H_8^+$ system[7] and for various $C_8H_9^+$ isomers,[8] both of which were in remarkable agreement with experiment, and an equally successful study of 1,2 hydrogen loss from various gaseous cations.[9]

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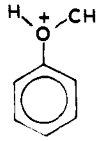
and other groups by 1,2 shifts in arenium ions have long been known to take place with great ease. While the ortho (**15**, **19**) and para (**17**) methoxybenzenium ions should be more stable than the meta isomers (**16**, **18**), migration via **18** may well not require too much energy. In any case the combination of **10** with methanol to form **14** must be very exothermic.

To test this mechanism, we have carried out detailed MINDO/3[16] calculations. We first confirmed the quoted[10,11] difference in energy (44 kcal/mol.) between **4** and **5** because no details had been published. Next we carried out calculations for the isomers **20**–**23**, obtained by protonating anisole in various positions. Their heats of formation and the corresponding proton affinities are shown in Table I, with values for methanol and benzene for comparison. Finally we calculated minimum-energy reaction paths (MERP) for the interconversions of **20**–**23**. The results are shown schematically in Figure 1.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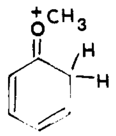
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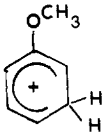
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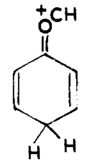
23

The addition of methanol to **5** is extremely exothermic (ΔH_{calcd}−45 kcal/mol). In solution, however, this excess energy will be lost very rapidly. Since the barrier to rearrangement of **21** is quite large (26 kcal/mol) and since methanol is a stronger base than anisole in the liquid phase, the proton will be lost from **20** or **21** before it has time to migrate further. Consequently the sole product from **6** in methanol solution is **7**. In the gas phase, however, methanol is a weaker acid than anisole (Table I), and the excess energy of **20** will not be dissipated nearly so fast. It is therefore not at all surprising that tritium migration occurs. However, since migration of tritium involves a number of consecutive 1,2 hydrogen shifts, including at least three crossings of the intervening energy barriers (Figure 1), and since in each of the relevant steps there will be a large kinetic isotope effect favoring migration of hydrogen over that of tritium, it is unlikely that equilibrium will be achieved. The proportion of para isomer (**7**) in the product is therefore likely to be much greater than that corresponding to equilibrium, i.e., **7**/**8**/**9** = 1:2:2. Since **19** is formed via **18**, the ratio of **8**/**9** should also be greater than the equilibrium value (1:1) but the difference should be less because the barrier between **18** and **19** is low. The products would then be expected to be formed in the order **7** ≫ **8** > **9**, as in fact was observed.

Our suggested mechanism could be tested very easily by submitting pure **7** (formed in liquid methanol) to a source of protons in methanol in the gas phase under the conditions used in the reaction of **6**.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008), the Robert A. Welch Foundation (Grant F-126), and the National Science Foundation (Grant CHE78-03213).

Registry No. 4, 38815-08-6; **5**, 17333-73-2; **6**, 73728-29-7; **7**, 34650-00-5; **8**, 81617-35-8; **9**, 81617-36-9; **18**, 81643-51-8; **19**, 81643-52-9; **20**, 18223-09-1; **21**, 81617-37-0; **22**, 81643-53-0; **23**, 81617-38-1.

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Solid-State ^{13}C NMR Characterization of the Bonding Mode of the Thiocyanate Ion in Copper(I) Complexes

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Received January 15, 1982

The ability of the thiocyanate ion to function as an ambidentate ligand has been the topic of considerable synthetic and structural investigations for over 20 years.[1] A wide variety of spectroscopic techniques have been applied to determine S vs. N bonding in thiocyanate complexes, including infrared,[1] Raman,[1] and X-ray photoelectron spectroscopy.[2] Two elegant magnetic resonance techniques were recently introduced by Fultz et al.[3,4] involving NQR and Kargol et al.[5] involving solution-state ^{13}C NMR.

Kargol et al.[5] have shown that the ^{13}C shift of the thiocyanate ligand is diagnostic of its bonding mode. In most cases examined by these authors, the S- and N-bound thiocyanate signals in the solution state are shifted to the higher- and lower-field side of ionic thiocyanate, respectively. We report here preliminary solid-state high-resolution ^{13}C NMR results for two Cu(I) complexes that demonstrate that analogous structural assignments can be made in the solid state by using cross-polarization magic-angle spinning (CP/MAS). The experiments were performed on a multinuclear solid-state NMR spectrometer designed and built in-house.[6] An interrupted decoupling sequence, first suggested by Opella and Frey,[7] was used to suppress signals from protonated carbons. All compounds studied were ca. 90% enriched in [^{13}C]SCN$^-$. The contact times (5 ms) were somewhat longer than typical (1–2 ms), since no protons are located in the immediate vicinity of the thiocyanate ion.

Figure 1a shows the spectrum of potassium thiocyanate taken with conventional pulsed FT NMR and magic-angle spinning. A sharp line (<10 Hz) is observed, with no evidence of ^{14}N quadrupole-induced splittings[8,9] and a remarkably short ^{13}C relaxation time (~3 s). The ^{13}C spectrum of [^{13}C]KSCN without spinning is shown in Figure 1b. Again, quite surprisingly, a narrow (~10 ppm) and only slightly anisotropic line is observed. Taken together, the data indicate that the SCN$^-$ ion in solid KSCN is undergoing fast rotational and/or translational motion. The chemical shift of the SCN$^-$ ion is 134 ppm downfield from Me_4Si, with the Delrin spinner signal taken to be at 90 ppm. This value is (coincidentally) identical with the chemical shift of the thiocyanate ion observed in aqueous KSCN solution.[5]

The bonding mode of the thiocyanate ligand was studied in the complexes CuL(CNS)[10] [L = $CH_3C(CH_2PPh_2)_3$ (I), $PhP(CH_2CH_2PPh_2)_2$ (II)]. Infrared and ^{1}H NMR studies of I have shown that this complex contains both Cu–SCN and Cu–NCS linkages in the solid state but exclusively Cu–NCS bonding in solution.[11]

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(1) This subject is most recently reviewed in Burmeister (Burmeister, J. L. In "Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives"; Newman, A. A., Ed.; Academic: London, 1975; pp 68-130.

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