purely theoretical standpoint is still at a very crude stage, measurement of anisotropic shielding can clearly provide a qualitative picture of the differences in bonding in organometalic compounds. Further investigation of such compounds from both experimental and theoretical views seems warranted and may prove fruitful in understanding their chemical properties.

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Unimolecular Reactions of Ionized Methyl Acetate and Its Enol: Mechanism for the Enol to Keto Isomerization

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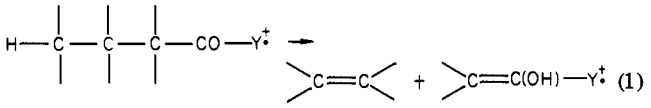
Abstract: Both the methyl acetate molecular ion and its enol fragment by loss of $CH_3O\cdot$ and show identical kinetic energy releases for decompositions occurring in the first drift region of a double-focusing mass spectrometer, consistent with fragmentation from the same structure. However, collisional activation mass spectra indicate that both keto and enol ions of lower energies retain their original structures. For fragmentation reactions occurring in the ion source, a study of methyl-d_3 acetate confirms that the methoxy group is lost directly in this fragmentation, while examination of the labeled enol ions $CD_2C(OH)OCH_3^{+\cdot}$ and $CH_2C(OH)OCD_3^{+\cdot}$ show that the methoxy neutral lost contains largely the enol hydrogen and two of the methoxy hydrogens. The results indicate that the enol structure does not fragment directly but isomerizes to the keto structure by two consecutive [1,4]-hydrogen shifts rather than by a direct [1,3]-hydrogen shift. With increasing lifetime methyl acetate molecular ions show extensive interchange of hydrogens between the two methyl groups; the extent of hydrogen interchange is less for the enol structure, presumably due to their different distribution of internal energy values. A detailed potential energy profile for the unimolecular reactions of the two structures is constructed.

A ubiquitous rearrangement of carbonyl compounds, eq 1,



(1)

results in the formation of the ionized enol of >C(H)—CO—Y as the product ion. The evidence supporting the specificity of the γ-hydrogen transfer and the initial enolic structure of the product has been amply reviewed.[2]

The question of the ketonization of the enol structure, >C=C(OH)$Y^{+\cdot}$ → >C(H)—CO—$Y^{+\cdot}$, also has received considerable attention, with mixed results. A number of studies[2,3] have presented evidence that, at least in the specific systems studies, ketonization does not occur prior to fast unimolecular reactions occurring in the ion source. The stable $C_3H_6O^{+\cdot}$ rearrangement product from 2-hexanone retains the enol structure,[4,5] and a wide variety of enolic ions are more stable thermodynamically than their corresponding keto ions.[6] On the other hand, Bursey et al.[7] have shown that the enol ion obtained from dissociative ionization of 2-*n*-propylcyclopentanone isomerizes slowly to the keto structure as its lifetime in an ICR spectrometer is increased from 10^{-3} to 10^{-1} s. The enolic $C_3H_6O^{+\cdot}$ and $C_4H_8O^{+\cdot}$ ions formed from alkanones have been shown[5,8] to rearrange to the keto form prior to fragmentation in the drift regions of a mass spectrometer. Of particular interest in the present context is the observation[8] that low-energy, $C_4H_8O^{+\cdot}$ enolic ions do not rearrange to the ketonic structure to a significant extent by the direct [1,3]-hydrogen shift (eq 2) but rather rearrange either by two consecutive [1,4]-hydrogen shifts (eq 3) or by a [1,2]-H shift followed by a [1,4]-H shift (eq 4). This work also showed that the direct shift (eq 2) became more important at higher internal energies, suggesting a high activation energy, but a more favorable energy-independent term, for the direct [1,3]-H shift.

$$CH_2{=}C(OH){-}CH_2CH_3^{+\cdot} \rightarrow CH_3{-}CO{-}CH_2CH_3^{+\cdot} \quad (2)$$

$$CH_2{=}C(OH){-}CH_2CH_3^{+\cdot} \rightarrow CH_3{-}C(=O^+H){-}CH_2CH_2\cdot \rightarrow CH_3{-}CO{-}CH_2CH_3^{+\cdot} \quad (3)$$

$$CH_3{-}C(OH){=}CHCH_3^{+\cdot} \rightarrow CH_3{-}C(=O^+H){-}CH_2CH_2\cdot \rightarrow CH_3{-}CO{-}CH_2CH_3^{+\cdot} \quad (4)$$

More recently Schwarz and Wesdemiotis[9] have reported that the structurally similar ion $CH_2{=}C(OH){-}OCH_3^{+\cdot}$, the enol form of ionized methyl acetate, isomerizes to the keto form by a sym-

(1) (a) Recipient of Canada–Hungary Cultural Exchange Fellowship, 1977–1978. (b) University of Toronto. (c) Cornell University.

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(9) Schwarz, H.; Wesdemiotis, C. *Org. Mass Spectrom.* **1979**, *14*, 25. Although this study reports that both ionized methyl acetate and its enol lose the intact methoxy group without isotopic exchange, a reinvestigation (Schwarz, H., private communication) provides results in essential agreement with those reported in Table I.

0002-7863/81/1503-36$01.00/0

Table I. Metastable Ion Spectra of Labeled $C_3H_6O_2^{+\cdot}$ Isomers

		rel abundance[a]				
m/z	ion	ion source	m_1*[b]	m_2*[b]	m_2*[c]	ran-dom[d]
		$CH_3COOCD_3^{+\cdot}$				
43[e]	$C_2H_3O^+$	95.0	19.7	9.2		5
44	$C_2H_2DO^+$	4.0	60.0	46.0		45
45	$C_2HD_2O^+$	0.8	19.8	40.2		45
46	$C_2D_3O^+$	0.2	0.5	4.6		5
		$CD_2{=}C(OH)OCH_3^{+\cdot}$				
43	$C_2H_3O^+$	4.0	4.0	8.0		20
44	$C_2H_2DO^+$	18.0	29.0	46.0		60
45	$C_2HD_2O^+$	78.0	67.0	46.0		20
		$CH_2{=}C(OH)OCD_3^{+\cdot}$[f]				
43	$C_2H_3O^+$	6.7	2.8	2.8	4.7	5
44	$C_2H_2DO^+$	91.5	82.0	62.3	54.0	45
45	$C_2HD_2O^+$	0.9	14.0	32.0	36.2	45
46	$C_2D_3O^+$	0.8	1.1	2.9	5.1	5

[a] Intensities as a percent of total $C_2(H,D)_3O^+$ ions measured with the MS-902. [b] m_1* and m_2* represent fragmentations occurring in the first and second drift regions, respectively. [c] Ion-accelerating potential 2 kV instead of 8 kV; 4-kV values for $CH_2{=}C(OH)OCD_3^{+\cdot}$ at *m/z* 43–46 were 3.3, 57.0, 34.6, and 5.0. [d] Calculated intensities assuming complete H/D randomization. [e] *m/z* 42 is <0.5% in the d_0 isomer. [f] Values for m_2* from the RMU-7 for *m/z* 43–46 were 5, 59, 32, and 4.

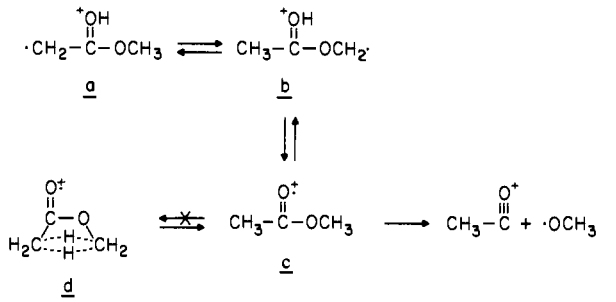
metry-forbidden [1,3]-hydrogen shift in a rate-determining step with a high activation energy.[10] However, the energetics data upon which this conclusion was partly based have been shown to be incorrect.[6] The results reported here are not consistent with a direct [1,3]-hydrogen shift but rather indicate that the enol form of ionized methyl acetate ketonizes by two consecutive and reversible [1,4]-hydrogen migrations, analogous to eq 3.

Results and Discussion

Both the methyl acetate molecular ion and its enol (derived from methyl *n*-pentanoate or methyl *n*-hexanoate) show metastable peaks corresponding to loss of CH_3O. Our results show identical and small kinetic energy releases ($T_{0.5}$ = 14 ±1 meV) for the metastable peaks from the two ions. Holmes and Lossing[6] also have observed identical shapes for the two metastable peaks with the same kinetic energy releases ($T_{0.5}$ = 15 + 0.7 meV). These results are consistent with, but do not necessarily require, identical structures for the fragmenting ions. The definitive evidence comes from isotopic labeling experiments.

Although fragmentation of the methyl-d_3 acetate molecular ion in the ion source leads predominantly (~95%) to loss of CD_3O·, as the lifetime of the ion increases, there is substantial H/D interchange between the two methyl groups. This is shown by the data in Table I which records the relative $C_2(H,D)_3O^+$ ion intensities observed as a result of fragmentation occurring in the ion source, in the first drift region, and in the second drift region of a double-focusing MS-902 mass spectrometer. For the long-lived ions fragmenting in the second drift region the relative intensities observed, $[C_2H_3O^+]$:$[C_2H_2DO^+]$:$[C_2HD_2O^+]$:$[C_2D_3O^+]$ = 9:46:40:5, are close to the relative intensities (5:45:45:5) anticipated for complete randomization of the H/D bonded to the two methyl groups. An effect of lifetime on keto ion randomization was also shown in an early study;[10] the faster randomization of $CD_3COOCH_3^{+\cdot}$ vs. $CH_3COOCD_3^{+\cdot}$ was attributed to an isotope effect, $k_H/k_D \approx 1.1$.[11] The collisional activation (CA) spectra[12] of nondecomposing $CH_3COOCH_3^{+\cdot}$ and $CH_3COOCD_3^{+\cdot}$ ions (Table II) show that the loss of CH_3O· involves a degree of scrambling that is intermediate between that occurring in competition with ion source decompositions and that prior to metastable decomposition, paralleling observations of previous studies.[13]

Scheme I



Fragmentation of the enol ion, $CD_2{=}C(OH)OCH_3^{+\cdot}$, derived from $C_4H_9CD_2$–CO_2CH_3, shows (Table I) considerable specificity for loss of CH_3O· for ions fragmenting in the ion source, although less than that for the keto isomer. However, the increase in H/D interchange with increasing lifetime is not as great for the enol as the keto; increasing the ion lifetime by reducing the ion accelerating potential was necessary to approach complete H/D randomization of $CH_2{=}C(OH)OCD_3^{+\cdot}$ ions. Data for these ions also show that this preferred loss of CH_3O· does *not* involve the original methoxy group of the enol ion. Fragmentation reactions occurring in the ion source result predominantly in loss of CD_2HO· rather than CD_3O·, and this preference is still observable for ions fragmenting after CA and in the first and second field free regions.

The low value (7%) for loss of CD_3O· from $CH_2{=}C(OH)$-$OCD_3^{+\cdot}$ indicates that direct fragmentation of the enol ion, eq 5, makes at most a small contribution even for ions of high internal

$$CH_2{=}C(OH)OCH_3^{+\cdot} \rightarrow CH_2{=}C{=}O^+H + CH_3O\cdot \quad (5)$$

energy. This is in agreement with the kinetic energy release results, discussed above, which can be best rationalized in terms of ketonization of the enol prior to fragmentation. Moreover, the labeling results also rule out the direct [1,3]-hydrogen shift as the route for ketonization as this should lead for the enol to specific loss of the original methoxy group on fragmentation (eq 6).[14]

$$CH_2{=}C(OH)OCH_3^{+\cdot} \rightarrow CH_3{-}CO{-}OCH_3^{+\cdot} \rightarrow CH_3{-}CO^+ + CH_3O\cdot \quad (6)$$

These results indicate that the mechanism of ketonization of the methyl acetate enol **a** to the keto form **c** can most readily be pictured as involving two sequential [1,4]-hydrogen shifts (Scheme I), a mechanism similar to that proposed for ketonization of $C_4H_8O^{+\cdot}$ enol ions[8] (eq 3). In the absence of any further hydrogen exchange reactions the two [1,4]-hydrogen shifts **a** → **b** and **b** → **c** would lead, on fragmentation of **c**, to specific loss of CH_3O· from $CD_2{=}C(OH)OCH_3^{+\cdot}$ and of CD_2HO· from $CH_2{=}C(OH)$-$OCD_3^{+\cdot}$ (major products of Table I).

As reported previously,[9] collisional activation (CA) mass spectra (Table II) show that the nondecomposing **a** and **c** ions have different structures. In addition, the CA spectra of these ions and their deuterated derivatives demonstrate that **a** and **c** ions of internal energies below that required for decomposition do not undergo appreciable isomerization. Lowering the ionizing electron energy should reduce the tendency of the resulting **a** and **c** ions to isomerize. This has little effect on the CA spectra of these ions, indicating that no significant proportion of isomeric ions is formed using 70-eV electrons. (Recently Wesdemiotis[15] has prepared ion

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(14) As an alternative for symmetry-forbidden [1,3]-H tautomerizations of radical cations, a mechanism of two consecutive [1,2]-H shifts has been proposed: Splitter, J. S.; Calvin, M. *J. Am. Chem. Soc.* **1979**, *101*, 7329. However, this mechanism is also ruled out by the data reported here.

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Table II. Collisional Activation Spectra of Labeled $C_3H_6O_2^{+\cdot}$ Isomers[a]

	CH_3COOCH_3			CH_3COOCD_3		$CH_2=C(OH)OCH_3$			$CD_2=C(OH)OCH_3$	$CH_2=C(OH)OCD_3$	
m/z	lit.[b]	70 eV	15 eV	70 eV	15 eV	lit.[b]	70 eV	13 eV	70 eV[c]	70 eV	13 eV[d]
13	1.5	1.4	2	1	1	1.4	1.0	1	0.2	1.0	2
14	5.0	5.7	5	2.5	3	5.0	5.1	5	1.3	3.6	5
15	7	11.0	11	5.5	6	7.5	9.6	10	5.5	3.0	5
16				5.0	6				4.5	2.2	3
17				4.0	5				5.0	1.2	2
18				2.0	2				0.2	6.8	6
26	5	2.5	3	1.9	2	4.3	2.7	3	1.1	1.3	3
27	7	5.9	6	2.7	3	6	5.3	6	2.3	1.6	3
28		2.5	4	4.5	4		2.9	4	5.4	3.7	5
29	30	22	18	7.5	7	24	17	16	11	11	10
30		3	6	14	14		4	6	7.2	12	13
31	20	28	25	4.5	5	19	26	22	25	4	5
32		<0.5		6.2	6		<0.5		3.1	5	5
33				9.2	8				4.9	16	12
34				11	11				1.1	0.9	1
41[e]	2.5	8	18	4	4	5	10	10	1	6	7
42	55	67	52	35	35	71	75	65	5	65	45
43	312	760	500	160	90	153	400	210	35	30	20
44	21	30	28	175	110	14	16	12	160	300	80
45	18	35	27	70	45	20	21	18	300	80	15
46		<1		20	17		<1		15	7	4
47				3	4				5	3	3
48				2	2				<1	3	3
57		<0.5		<0.3			0.2	<0.5	<0.5	0.2	<2
58	5	5.1	5	0.3	<0.5	11	14	14	0.5	14	10
59	13	10	10	5.0	4	6.4	5.9	5	15	1.0	1
60	1.0	3.3	3	1.5	1	9.3	5.2	6	5.5	2.0	4
61				3.0	2				0.5	2.5	3
62				8	7				0.5	1.5	4
63				1.0	1					6	5

[a] Intensities as a percent of total ion abundance, excluding m/z 40–48, measured on the RMU-7. [b] Reference 9; data shown there as m/z 40 are given here as m/z 41, as our data show m/z 40 abundance <1. [c] Data at 17 eV are the same as those at 70 eV within the large experimental error. [d] Data for m/z 57–63 were poorly reproducible. [e] Abundances inaccurate due to poor resolution.

b from $CH_3COOCH_2OCH_3$, and its CA spectrum is significantly different from that of **a** or **c**.) The insensitivity of the CA of labeled **c** ions to ionizing electron energy shows that there is no separate low-energy pathway for hydrogen exchange in **c** such as through the bicyclic transition state **d**; a similar intermediate was proposed by Yeo[11] for H/D interchange in the ethyl acetate molecular ion.

Based on these arguments and the energetics data of Holmes and Lossing,[6] we have constructed in Figure 1 a potential energy profile for the unimolecular fragmentation of the methyl acetate molecular ion and its enol; $\Delta H_f°$(**a**) = 114 kcal mol^{-1},[6] $\Delta H_f°$(**c**) = 138 kcal mol^{-1},[16] and $\Delta H_f°(CH_3CO^+ + \cdot OCH_3)$ = 152.5 kcal mol^{-1}.[6,17] $\Delta H_f°(CH_2{=}C{=}OH^+ + \cdot OCH_3)$ = 171 ± 8 kcal mol^{-1} was derived from the estimate by Beauchamp[19] that the oxygen proton affinity of ketene is 18 ± 8 kcal mol^{-1} less than the carbon proton affinity. $\Delta H_f°$(**b**) = 116 kcal mol^{-1} if $D(CH_3COOCH_2{-}H)$ = 95 kcal mol^{-1} and the proton affinities of the carbonyl oxygen in $CH_3COOCH_2\cdot$ and in methyl acetate (195 kcal mol^{-1})[20] are similar; $\Delta H_f°$ of **a** should be significantly lower than that of **b** because of the resonance stabilization of the radical site in **a**.[2]

The high tendency for hydrogen scrambling in both **a** and **c** before metastable decomposition by loss of $\cdot OCH_3$ from **c** indicates that the effective activation energy for the tautomerization **a** → **c** is somewhat less than ~38 kcal mol^{-1}, as shown in Figure 1. This is considerably lower than the activation energy (~57 kcal mol^{-1}) for direct fragmentation of the enol to $CH_2{=}C{=}OH^+ + \cdot OCH_3$, and it is not surprising that this fragmentation route is not observed. The fact that the enol **a** does not convert directly to the keto **c** by a [1,3]-hydrogen shift implies that the energy barrier for this symmetry-forbidden reaction must be considerably greater than 38 kcal mol^{-1}. This conclusion is consistent with the recent ab initio calculations[21] of a barrier of 85 kcal mol^{-1} for conversion of vinyl alcohol to acetaldehyde by a [1,3]-hydrogen shift.

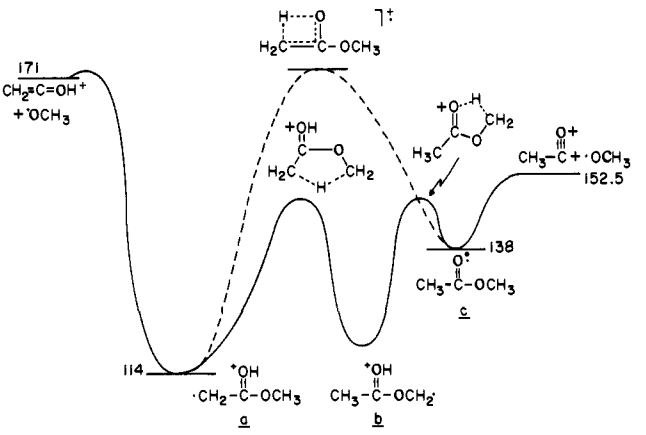

Figure 1. Potential energy profile (ordinate, kcal mol^{-1}) for unimolecular reactions of ionized methyl acetate (**c**) and its enol (**a**).

This mechanistic scheme must also be consistent with the observation that metastable **a** ions undergo less complete H/D scrambling before dissociation than do the corresponding **c** ions. Under the assumption of the quasi-equilibrium theory, the degree of such scrambling of **c** ions is determined by their internal energy,

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(17) It should be noted that this value, derived from appearance energies,[6] leads to an enthalpy of formation of the acetyl cation of 153 kcal mol^{-1} which is ~7 kcal mol^{-1} lower than that derived[18,19] from measurements of the proton affinity of ketene.

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independent of whether they are formed by molecular ionization or isomerization from **a**. Thus such data would result if the metastable **a** and **c** ions are formed with substantially different distributions of internal energy values (which will not necessarily affect appreciably the kinetic energy released in metastable decomposition).[22] The low proportion of **a** ions formed with the low energy required for complete scrambling could be due to a low-energy dissociation of the molecular ion which competes with formation of such **a** ions. In support of this, Wesdemiotis[15] has recently shown that metastable **a** ions prepared from different precursors show substantial variations in their extent of scrambling. At ion lifetimes giving 95% scrambling of **c** from CD_3COOCH_3, **a** ions from $(CH_3)_2CHCH_2CH_2COOCD_3$ show 81% scrambling, while **a** ions from $DOCH_2CH_2COOCH_3$ show 72% scrambling.

Conclusion

The potential energy surface involving ions **a**, **b**, and **c** is unique in that the energy barriers for the [1,4]-H isomerizations **a** $\rightleftarrows$ **b** and **b** $\rightleftarrows$ **c** are nearly the same as the barrier for the major dissociation pathway **c** $\rightarrow$ CH_3CO^+. However, the reasons for this behavior appear to be generally applicable to other tautomeric systems. Enolic ions are generally more stable than their ketonic isomers, both in terms of the lower heat-of-formation values of enols[6] and the more facile α-cleavage dissociation of keto isomers.[2-5,8] The latter will thus also provide a favored dissociation channel for an enol *if* isomerization to its keto isomer is facile. The [1,4]-H shift provides such a path here, while the symmetry-forbidden [1,3]-H shift has a much higher activation energy.[5,8,21,23] For these $C_3H_6O_2^{+\cdot}$ ions the [1,2]-H shift[14] is also much less facile than the [1,4]-H shift, although it is favored over the [1,3]-H isomerization in specific cases[23] such as eq 4.[8] There is no evidence for concerted hydrogen exchange such as isomerization through the bicyclic transition state **d**.[11]

Experimental Section

Mass spectra were recorded on AEI-MS-902 and reversed-geometry Hitachi RMU-7[24] mass spectrometers, both operated at 8-kV ion acceleration, 70-eV electron energy, and source temperatures of 120-150 °C unless indicated otherwise. Samples were admitted through all-glass heated inlet systems. For the MS-902, fragmentation reactions occurring in the first drift region (between the source and electrostatic sector) were observed by scanning the accelerating voltage at constant electrostatic sector voltage using a β (energy-defining) slit width of 0.008 in. The kinetic energy releases reported were obtained from the width at half-height after correction for the main beam width. Fragmentation reactions occurring in the second drift region were evaluated from the metastable peaks in the normal mass spectra. CA spectra, obtained as described previously,[24,25] were the averages of several multiscan runs on the RMU-7.

Methyl hexanoate-2,2-d_2 and methyl-d_3 acetate were obtained from Merck, Sharp, and Dohme, Montreal, while methyl-d_3 pentanoate was prepared by esterification of pentanoic acid with methyl-d_3 alcohol.

Acknowledgment. The authors are indebted to the National Research Council of Canada and the National Institutes of Health (Grant GM16609) for financial support, to Dr. C. Wesdemiotis for key recent experiments, to Professor J. L. Holmes for communication of results prior to publication, and to Professor H. Schwarz for helpful correspondence.

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The Isolated Molecule Approach. Theoretical Studies of the Inductive Effect

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Abstract: The proton affinities of a variety of ω-substituted alkylamines, determined by ab initio molecular calculations, have been shown to be in rough accord with the operation of an electrostatic field effect. Calculations using isolated molecules, one having the probe attached and one the substituent, are in excellent agreement with such a field effect and indicate that any through-bond inductive transmission is insignificant in the systems investigated. The isolated molecule approach is used to estimate the magnitude of the direct field effect in the proton affinities of substituted amines.

There is continued interest[1-5] in the mechanism of transmission of polar effects in σ-bonded systems. The two major mechanisms that have been considered[2,6] are the field effect, a direct through space electrostatic interaction, and the σ-inductive effect, a progressive but diminishing relay of polar effects along a chain of carbon atoms. Although field effects appear to predominate in many examples,[2,3,6,7] there is evidence[1,3] for an additional transmission mode, particularly over short distances.

One of the major problems in experimental investigations of the transmission of polar effects is to obtain a sufficient variety of systems of fixed geometry. Great ingenuity and effort have been put into the synthesis of model compounds,[6,7] but the flexibility of many molecules and the difficulty of obtaining a reasonable range of substituents in others have provided severe limitations.

By contrast, theoretical calculations can be made for many different geometries by using fixed conformations of aliphatic

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