mediate set of force constants for the hydronium ion. The fitting involved the adjustment of *four* valence-bond force constants. The frequencies corresponding to this adjusted set of force constants were employed for barrier calculations. The bond-stretch and angle-bond force constants calculated using these frequencies and the simple Herzberg treatment, neglecting interaction terms,[3] are nearly identical for H_3O^+ and D_3O^+ but are lower than those obtained using a more complete expression for the potential energy. When the nearly identical force constants are employed to calculate V_i, the isotope effect is very small.

Complexes of *p*-Anisylethylenes. III. The Crystal Structure of the Dichloroiodate(I) Salt of the Tetra-*p*-anisylethylene Dication

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Abstract: The crystal structure of the dichloroiodate(I) salt of the tetra-*p*-anisylethylene dication was determined from single crystal X-ray diffraction data (film methods, visual estimates of intensity). The ICl_2^- anions exist as nearly linear groups (bond angle = 174.5 ± 3°) with I–Cl distances of 2.510 and 2.567 ± 0.006 A. The anisyl groups attached to the central carbon atoms of the dication are rotated 28.2° from planar orientation because of the *o*-hydrogen interaction. The two three-atom groupings of the central ethylenic carbon atom and its attached phenyl carbon atoms are not planar with each other in the dication, but make an angle of 41° with respect to each other. This apparent reduction of the π-bond order of the central C–C bond in the dication is consistent with the qualitative predictions of simple MO theory.

The X-ray single crystal study of tetraanisylethylene dichloroiodate(I) evolved from earlier work in a series concerning complexes of halogens with organic compounds.[1,2] The physical methods usually used to establish the identity of an organic species, such as freezing point depression, infrared, visible, and ultraviolet spectra, and nmr were used to categorize the dication species and are outlined in a subsequent paper of this series. Although these methods gave very strong evidence for the existence of the tetraanisylethylene (TAE) dication, the evidence of this type for the existence of a dicationic species has frequently been questioned. Therefore, the structure determination was undertaken to give independent evidence for the existence of the dication in the solid state and, at the same time, to determine the detailed geometry of the dication.

Experimental Details

Dark blue-green crystals of the TAE complex were grown slowly by illumination (sunlight) of a carbon tetrachloride solution of tetraanisylethylene and iodine present in a mole ratio of 1:2.[3] The identity of the product was confirmed by infrared spectra and chemical analyses. *Anal.* Calcd: C, 42.5; H, 3.3. Found: C, 43.57; H, 3.62. The crystals were quite stable in air.

The cell constants were obtained from two different types of measurements. One set was obtained by a least-squares fit to data obtained from a forward reflection DeWolff–Guinier camera powder diagram (a = 9.802 ± 0.007, b = 10.937 ± 0.008, c = 16.865 ± 0.009 A, β = 114.54 ± 0.05°). The film was calibrated by a simultaneous exposure of a quartz sample. Independent values of a and b were obtained from back-reflection Weissenberg single crystal diagrams using a least-squares extrapolation method to remove systematic errors (a = 9.797 ± 0.003, b = 10.962 ± 0.009 A). The averaged values of these monoclinic cell dimensions are a = 9.798 ± 0.003, b = 10.956 ± 0.004, c = 16.865 ± 0.009 A, β = 114.54 ± 0.05°.

The c axis extended in the direction of the needle axis of the crystals. Intensity data were obtained from equiinclination Weissenberg diagrams ($hk0$) to ($hk9$) taken with Cu Kα radiation, and Buerger precession camera diagrams ($0kl$) to ($5kl$) and ($h0l$) to ($h4l$) with Mo Kα radiation. Sufficient repeated visual estimates of the intensities were made so that a standard deviation in the mean intensity was calculated for each reflection. These standard deviations were later used to calculate the weights for the least-squares refinement of structure factors. The intensities were corrected for Lorentz and polarization factors. The specimens used for the intensity data were small enough in diameter so that for one crystal (μR = 0.19) absorption corrections were neglected, and for a second crystal (μR = 1.20) absorption corrections were made assuming a cylindrical rod-shaped specimen. A total of 1991 independent reflections were used. Characteristic absences were ($h0l$) with l odd, which indicates that the space group symmetry is either P2/c or Pc. The density, assuming two formula weights of $TAE[ICl_2]_2$ per cell, is 1.612, which agrees well with that measured experimentally by pycnometer, 1.65 g/cm^3.

Atom-scattering factors used in the structure factor calculation were taken from the "International Tables for Crystallography."[4] The Thomas–Fermi values were used for I, while the neutral atom values for Cl, C, O, and H were those based on self-consistent wave functions. Both the real and imaginary dispersion corrections were applied for I, Cl, and O (where applicable) in the final stages of refinement.

Full-matrix, least-squares refinements were carried out using a locally developed program for the IBM 7044. Several types of discrepancy factors were calculated: $R_1 = \Sigma|\Delta F|/\Sigma|F_o|$, $R_{1w} = \Sigma w|\Delta F|/\Sigma w|F_o|$, and $R_{1h} = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$.[5] The weighting scheme used was $w^{1/2} = 1/s_{(F)}$, where $s_{(F)}$ is the standard deviation

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(1) R. E. Buckles and W. D. Womer, *J. Am. Chem. Soc.*, **80**, 5055 (1958).

(2) R. E. Buckles, R. E. Erickson, J. D. Snyder, and W. E. Person, *ibid.*, **82**, 2444 (1960).

(3) Further details are given in the following paper of this series.

(4) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202, 211.

(5) W. C. Hamilton, *Trans. Am. Cryst. Assoc.*, **1**, 17 (1965).

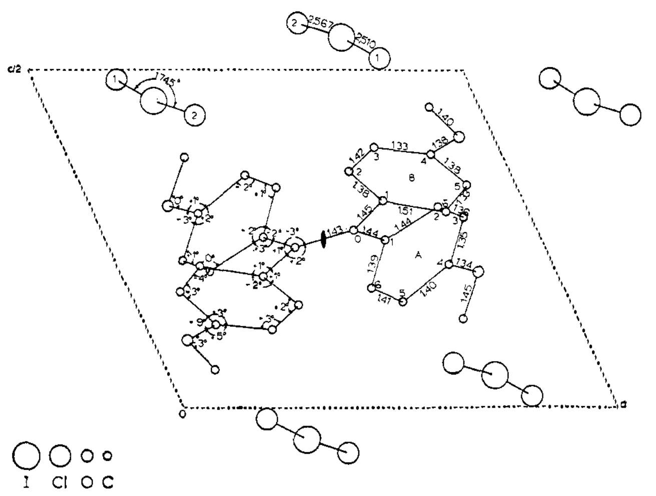

Figure 1. Projection of the structure of TAE$[ICl_2]_2$ onto (010). The interatomic distances are given in angstrom units. The bond angles in the TAE group are given as deviations from 120°.

in the mean value of the intensity estimates determined for each reflection. If reflections were observed too infrequently to determine a reliable estimate of the standard deviation, a standard deviation of 40% was arbitrarily assigned. Reflections below the minimum observable were given zero weight unless $|F_c|$ was greater than $|F_o|$, in which case they were given unit weight.

Structure Determination

The structure was solved from a three-dimensional Patterson map which clearly indicated the positions of the iodine and two chlorine atoms of the anion. The structure factors based on these positions (space group P2/c) gave a discrepancy factor, $R_1 = 0.29$. A three-dimensional electron density map calculated at this point revealed the approximate positions of all the carbon and oxygen atoms in addition to the chlorine and iodine atoms. Introduction of these atoms with isotropic temperature factors into the least-squares calculation dropped the discrepancy factor to 0.11. At this point equivalent reflections obtained with the same type of radiation were averaged, interlayer scale constants were fixed, and only an over-all scale factor was permitted to vary along with the coordinates of the atoms and anisotropic temperature factors.

An electron density difference map disclosed the positions of many of the hydrogen atoms, but the expected positions of all the hydrogen atoms were also calculated independently. Holding the H atoms in these fixed positions, the least-squares refinement was continued a few more cycles to produce the final discrepancy values, $R_1 = 0.106$, $R_{1w} = 0.084$, $R_{1h} = 0.11$, and the parameters listed in Table I. (It should be emphasized that the hydrogen atom positions were not determined from X-ray data, but were placed to give reasonable C–H bond lengths and orientations typical of phenyl and methoxy groups.) Calculated and observed structure factors are available.[6]

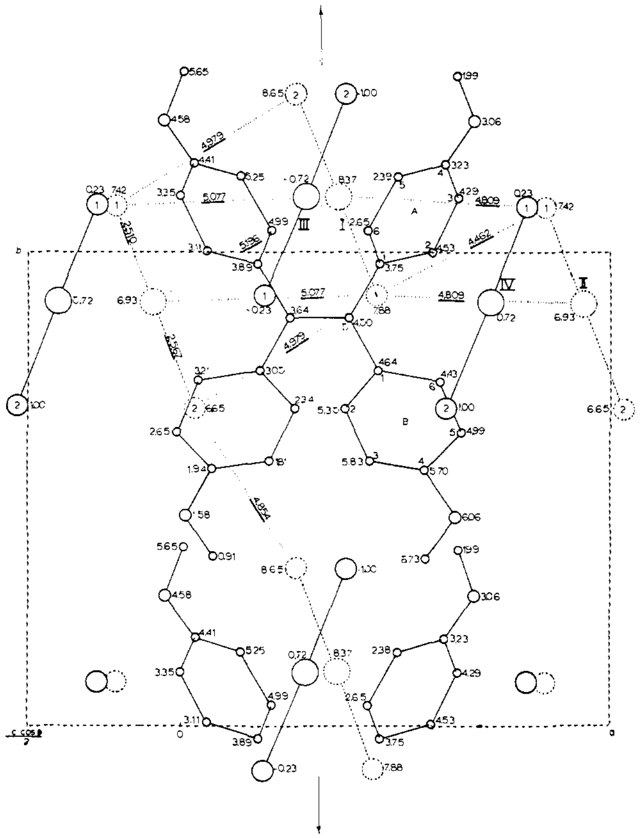

Figure 2. An orthogonal projection of the structure of TAE$[ICl_2]_2$ onto the (001) plane. Only a little more than one-half of the cell contents (from ~0 to ~$c/2$) have been shown in the projection. The perpendicular distances of the atoms from the (010) face of the unit cell are given in angstrom units by each atom. The distances between I and Cl atoms are given in angstrom units and are underscored (average error, Cl–Cl, ±0.009 A; I–Cl, ±0.007 A).

Discussion of the Structure

The structure of the dication can be conveniently discussed with reference to the projection on to (010) shown in Figure 1, the orthogonal projection on to (001) shown in Figure 2, and Table II which gives the interatomic distances and angles. The dichloroiodate(I) anion, ICl_2^-, is nearly linear (Cl–I–Cl bond angle = 174.5 ± 3°) and nearly symmetric (I–Cl bond distances are 2.510 and 2.567 ± 0.006 A). The standard deviation in the bond angle is large enough that the ion cannot be considered significantly different from linear.

The average I–Cl distance, 2.539 A, is in good agreement with the value of 2.55 ± 0.02 A found by Visser and Vos[7] in tetramethylammonium dichloroiodide. The I–Cl bond distance would be expected to be 2.34 A if it were a covalent single bond. A decrease in bond order to $^1/_2$, as suggested by the molecular orbital description of the bonding, would increase the predicted length to 2.52 A, in reasonable conformity with the observed value. The I–Cl distances are significantly different from each other. Asymmetry in XYX^- ions has been observed before,[8] and a theoretical discussion of this phenomenon[9] relates the deviation from symmetrical ions to the density of packing. Increased pressure from close packing by surrounding bulky cations was correlated to increased tendencies toward

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(6) A list of calculated and observed structure factors has been deposited as Document No. 9383 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(7) G. J. Visser and A. Vos, *Acta Cryst.*, **17**, 1336 (1964).

(8) R. C. L. M. Slater, *ibid.*, **12**, 187 (1959).

(9) J. C. Slater, *ibid.*, **12**, 197 (1959).

Table I. Atomic Parameters for Tetra-*p*-anisylethylene Dichloroiodate(I)[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
I	0.2494 (2)	0.1125 (1)	0.9530 (1)	153 (2)	90 (1)	41 (1)	11 (4)	57 (2)	−4 (2)
Cl_1	0.1867 (8)	0.9012 (5)	0.9847 (4)	205 (11)	111 (6)	41 (3)	−58 (13)	74 (11)	−12 (8)
Cl_2	0.3353 (8)	0.3280 (6)	0.9348 (5)	248 (13)	105 (5)	79 (5)	16 (14)	177 (14)	20 (9)
O_A	0.822 (2)	0.285 (1)	0.200 (1)	103 (23)	102 (15)	91 (13)	−21 (33)	71 (29)	57 (24)
O_B	0.928 (2)	0.443 (1)	0.396 (1)	137 (26)	103 (14)	60 (10)	79 (30)	57 (28)	109 (20)
C_D	0.579 (2)	0.856 (1)	0.261 (1)	108 (30)	74 (16)	7 (9)	7 (31)	3 (33)	−30 (20)
C_{1A}	0.641 (2)	0.967 (2)	0.245 (1)	25 (20)	96 (19)	15 (10)	−17 (33)	−30 (29)	12 (23)
C_{2A}	0.794 (2)	0.003 (2)	0.296 (1)	121 (32)	134 (25)	21 (12)	111 (53)	92 (35)	15 (26)
C_{3A}	0.846 (3)	0.112 (2)	0.280 (1)	228 (42)	23 (11)	54 (14)	−23 (45)	120 (42)	13 (30)
C_{4A}	0.761 (2)	0.181 (2)	0.211 (2)	135 (37)	83 (19)	46 (13)	−75 (42)	72 (40)	15 (27)
C_{5A}	0.613 (2)	0.149 (2)	0.156 (1)	23 (24)	96 (21)	51 (14)	16 (33)	18 (34)	71 (25)
C_{6A}	0.557 (2)	0.038 (2)	0.173 (2)	121 (34)	86 (19)	53 (14)	−6 (41)	100 (39)	60 (27)
C_{1B}	0.673 (2)	0.753 (1)	0.303 (1)	152 (32)	30 (13)	10 (9)	−53 (32)	71 (31)	−5 (16)
C_{2B}	0.627 (2)	0.667 (2)	0.346 (1)	89 (28)	52 (14)	36 (13)	72 (35)	39 (32)	8 (20)
C_{3B}	0.710 (2)	0.559 (2)	0.380 (1)	111 (33)	96 (18)	19 (10)	−27 (42)	69 (37)	28 (24)
C_{4B}	0.838 (3)	0.545 (2)	0.372 (2)	220 (47)	87 (19)	62 (15)	73 (48)	187 (49)	137 (30)
C_{5B}	0.888 (3)	0.626 (2)	0.326 (2)	173 (42)	96 (23)	47 (13)	20 (50)	114 (40)	27 (29)
C_{6B}	0.813 (2)	0.727 (2)	0.289 (2)	94 (35)	101 (23)	74 (18)	−56 (46)	78 (47)	−18 (33)
C_{MA}	0.734 (4)	0.368 (2)	0.130 (3)	211 (54)	151 (34)	140 (28)	−110 (69)	230 (72)	51 (51)
C_{MB}	0.886 (3)	0.350 (2)	0.439 (2)	200 (47)	57 (16)	72 (16)	110 (42)	123 (48)	1 (28)

	x	y	z	B		x	y	z	B
H_{2A}	0.848	0.946	0.348	3.7	H_{6B}	0.838	0.788	0.252	4.1
H_{3A}	0.932	0.067	0.322	3.3	H_{MA1}	0.628	0.394	0.141	6.5
H_{5A}	0.537	0.204	0.099	2.9	H_{MA2}	0.683	0.317	0.069	6.5
H_{6A}	0.441	0.082	0.134	3.9	H_{MA3}	0.782	0.445	0.117	6.5
H_{2B}	0.501	0.686	0.353	2.3	H_{MB1}	0.833	0.374	0.494	4.0
H_{3B}	0.650	0.488	0.413	3.0	H_{MB2}	0.748	0.319	0.398	4.0
H_{5B}	0.973	0.604	0.323	3.9	H_{MB3}	0.923	0.268	0.454	4.0

[a] Anisotropic temperature factor, $e^{-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})}$. All b values × 10^4. Estimates of the standard deviations in the last significant digit are given in parentheses.

Table II. Interatomic Distances (A) and Bond Angles (deg)[a]

$I–Cl_1$	2.510 (6)	$Cl_1–I–Cl_2$	174 (3)	$C_D–C_{D'}$	1.43 (4)	$C_{D'}–C_D–C_{1A}$	117 (2)
$I–Cl_2$	2.567 (6)					$C_{D'}–C_D–C_{1A}$	122 (2)
						$C_{1A}–C_D–C_{1B}$	121 (2)

	Ring A	Ring B		Ring A	Ring B
$C_1–C_2$	1.44 (3)	1.38 (2)	$C_6–C_1–C_2$	118 (2)	118 (2)
$C_2–C_3$	1.36 (3)	1.42 (3)	$C_1–C_2–C_3$	120 (2)	122 (3)
$C_3–C_4$	1.35 (3)	1.33 (3)	$C_2–C_3–C_4$	121 (2)	117 (2)
$C_4–C_5$	1.40 (3)	1.38 (3)	$C_3–C_4–C_5$	122 (2)	123 (3)
$C_5–C_6$	1.41 (3)	1.33 (3)	$C_4–C_5–C_6$	118 (1)	123 (4)
$C_6–C_1$	1.39 (3)	1.51 (3)	$C_5–C_6–C_1$	121 (2)	116 (2)
$C_D–C_1$	1.44 (3)	1.45 (2)	$C_D–C_1–C_2$	122 (2)	121 (3)
$C_4–O$	1.34 (3)	1.38 (3)	$C_D–C_1–C_6$	120 (2)	121 (2)
$O–C_M$	1.45 (4)	1.40 (3)	$C_5–C_4–O$	121 (1)	111 (3)
			$C_3–C_4–O$	117 (4)	125 (2)
			$C_4–O–C_M$	120 (3)	117 (3)

	Ring A			Ring B			
	$I_{(IV)}$	$Cl_{1(IV)}$	$Cl_{2(IV)}$	$Cl_{1(1)}$	$Cl_{2(1)}$	$Cl_{2(IV)}$	$I_{(IV)}$
C_1	4.00	5.03		3.64	6.45	4.07	5.52
C_2	4.23	4.92		3.70	5.15	4.90	5.78
C_3	4.39	4.34		4.28	4.18	5.29	5.57
C_4	4.21	3.66		4.65	4.87	4.93	5.83
C_5	3.93	3.69		4.66	6.24	4.06	6.95
C_6	3.76	4.40		4.26	6.96	3.49	6.27
O	4.96	3.69	4.75	5.69	4.74	5.67	5.12
C_M	5.47	3.78	3.48	6.27	3.62	6.74	3.73

Equations of planes in the form: $pi + qj + rk = d$ (in A)

					Deviation from plane								
	p	q	r	d	C_1	C_2	C_3	C_4	C_5	C_6	O	C_M	C_D
Ring A	0.6372	−0.4981	−0.5881	0.918	−0.04	0.04	−0.02	0.00	−0.00	0.02	0.03	0.09	0.05
Ring B	−0.1799	−0.4875	−0.8544	−8.770	−0.03	0.00	0.02	−0.02	−0.00	0.03	0.09	0.14	−0.09
C_D, C_{1A}, C_{1B}	0.2859	−0.3500	−0.8920	−5.752	[designate this plane as P]								

Angle between normals to ring A and plane P = 28.2°
Angle between normals to ring B and plane P = 28.2°
Angle between normal to plane P and its equivalent, P′, after rotation by the twofold axis = 41.0°
Angle between normal to plane P and the b axis = 20.5°

[a] Estimates of the standard deviation in the last significant digit are given in parentheses.

symmetrical ions. The I–Cl bond-length differences here, however, are small compared to the deviations found in the unsymmetrical triiodide ions. As a result, the dichloroiodide group can be considered as a normal anion which is nearly symmetrical. Since there are four anions per cell and only two TAE cationic groups, it follows that the TAE groups are dications.

The structure of the cationic group can be logically discussed in terms of its distortion from a hypothetical planar tetraanisylethylene molecule. Such a molecule could possess three mutually perpendicular twofold axes of rotation. One of these twofold axes lies in the plane of the molecule and is perpendicular to the central double bond. This is the only twofold rotation axis which is conserved in the distortion to the real cation. The projection shown in Figure 1 is along this twofold axis; the idealized planar molecule would have all of its atoms lying along a single straight line in this projection.

The real molecule cannot be planar because of the interaction of the *o*-hydrogen atoms of the phenyl groups. This interaction causes the phenyl groups to twist about the C_D–C_{1A} or C_D–C_{1B} bonds 28.2° for both ring A and ring B. The phenyl rings are planar; deviations from the best least-squares planes average about 0.02 for each ring. The carbon atom, C_D, also lies in the same plane as each of the benzene rings. The oxygen and carbon atoms of the methoxyl groups, however, are displaced slightly from the plane of the phenyl group to which they are attached.

One further distortion from a planar arrangement still exists. In the idealized molecule, carbon atoms C_D, C_{1A}, and C_{1B} would be coplanar with the equivalent atoms related by the twofold rotation axis, and all six atoms would lie on a straight line in projection—the projection of the sp^2 plane of the olefin. In the TAE dication, however, the two groups of atoms are no longer coplanar, but the normals of the two planes make an angle of 41.0° with respect to each other (or 20.5° with respect to the normal of the idealized plane). Since the normals of these planes are in the approximate direction expected for the p orbitals involved in π bonding of an olefinic group, one would expect a considerable reduction in the double bond character of the central C–C bond of the molecule. Molecular orbital calculations[10] on tetraphenylethylene give a π-bond order of 0.685 for the central double bond of the normal molecule and 0.187 for the same bond after the loss of two electrons. Thus, it would appear that, qualitatively, a rather low double bond order is to be expected for this bond in the TAE dication. The bond distance observed for this bond is compatible with this point of view, but, unfortunately, the error in the bond distance is large enough that little significance ought to be placed in it or in the listed value of any of the C–C or C–O bond distances in Table II.

The C–C and C–O distances are reasonably close to the normal values, considering the magnitude of the standard deviations. The average C–C distance in the two benzene rings is 1.392 A for ring A and 1.391 A for ring B. The distances between the atoms of the dichloroiodide group and the atoms of the dication are all greater than 3.5 A, so that normal van der Waals distances appear to exist. The dichloroiodide groups are also well separated from each other (see Figure 2).

Summary

The crystal structure determination demonstrates the existence of a dicationic species in crystals of TAE-$[ICl_2]_2$. This demonstration makes it seem extremely plausible that the ion also exists in the solvents in which the spectral, nmr, and freezing point studies were made which are reported in a separate paper of this series.

Acknowledgments. This research was supported by a National Science Foundation grant (No. GP-3523) for which the authors are very grateful.

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[10] A. Streitwieser, Jr., J. I. Brauman, and C. A. Coulson, "Supplemental Tables of Molecular Orbital Calculations," Vol. II, Pergamon Press, New York, N. Y., 1965, p 1134.

Nuclear Magnetic Resonance Studies of a Radical–Radical Dimerization Reaction[1]

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Abstract: We have studied the kinetics of a reaction involving the dissociation of a diamagnetic dimer into two radicals. The reaction may be written as dimer $\rightleftarrows$ 2 radicals. Nuclear magnetic resonance spectroscopy was used to determine rate constants. The equilibrium constant and thermodynamic parameters were determined. A second reaction, involving rearrangement of the dimer, was also studied. The two reactions have the same activation energies but different rate constants.

Nuclear magnetic resonance spectroscopy may be used to study the kinetics of reactions at equilibrium. Characteristic changes in the nmr line shape which occur with composition or with temperature can be used to determine lifetimes and rate constants. Nmr has been used to study the kinetics of numerous types of exchange reactions between diamagnetic materials.[2] These techniques have also been used to

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