A Nuclear Magnetic Resonance and X-Ray Diffraction Study on the Metal Salt Complexes of Dicarbonyl-stabilized Ammonium and Sulphonium Ylides

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The metal salt complexes of some carbonyl-stabilized ammonium and sulphonium ylides were studied by n.m.r. spectroscopy and X-ray diffraction. The crystal structure of the trimethylammonium diformylmethylide (I)–NaClO$_4$ complex forms a continuous network between the octahedrally co-ordinated sodium cations, perchlorate anions, and the ylide molecules. The behaviour of $^3J(CHO,CHO)$ of (I) in solution reveals that the *trans,trans* structure, in which a metal cation is bound simultaneously to both formyl oxygens, is formed only to a very small extent, if at all. The $^1J(CHO)$ and chemical shift data for (I) indicate that the cations prefer to bond to oxygen, not to the ylide carbon, which is the preferred site in sulphonium ylides. The complex formation free energies (at 25 °C in acetone) range between −5.0 and 10.0 kJ mol^{-1}. The formation entropy for the AgBF$_4$ complex of 1-dimethylsulphonio-4,4-dimethyl-2,6-dioxocyclohexanide is *ca.* −85 J K^{-1} mol^{-1}.

There are a few papers on the complex formation between metal cations and carbonyl-stabilized ammonium[1–4] and sulphonium[5–7] ylides. The topic is interesting because it has been suggested that the ylides can be used as metal-cation carriers.[6] The complex formation can also be used to probe the conformational energetics of some ylides like (I)—(IV), as previously done for some substituted methylenemalonaldehydes.[8,9] The purpose of this study was to characterize structures and energetics of the complexes of dicarbonyl- and cyano-stabilized ammonium and sulphonium ylides, such as trimethylammonium diformylmethylide (I), dimethylsulphoniodicyanomethylide (II), dimethylsulphonio(cyano)methoxycarbonylmethylide (III), dimethylsulphoniodiacetylmethylide (IV) 1-dimethylsulphonio-2,5-dioxocyclopentanide (V) and 1-dimethylsulphonio-4,4-dimethyl-2,6-dioxocyclohexanide (VI).

The conformational energetics of the formyl groups in (I) are determined by the π-interactions between the sp^2 hybridized atoms and steric and Coulombic interactions between the terminal groups. The $^3J(^{14}N,^1H)$ coupling and its insensitivity to solvent[3] and the $^3J(^{13}CHO,C^1HO)$ couplings (this work), together with theoretical calculations,[4] show that the *cis,cis* arrangement of the formyl C=O group is the predominant conformation in (I). This can be accounted for by the Coulombic repulsion of the formyl oxygens in the *trans,trans* structure and the attraction between the carbonyl oxygen and the positively charged heteroatom in the *cis* structures. However, it is not ruled out that the formyl groups can be attracted to the *trans,trans* arrangement with a metal cation, as in the case of some methylenemalonaldehydes[8,9] (VII). As to the complex formation in these ylides, a metal cation may also bond to one *cis*-formyl group or to the negatively charged ylide carbon.

(I)

(II)

(III)

(IV)

(V)

(VI)

(VIIa)

trans, cis

(VIIb)

trans, trans
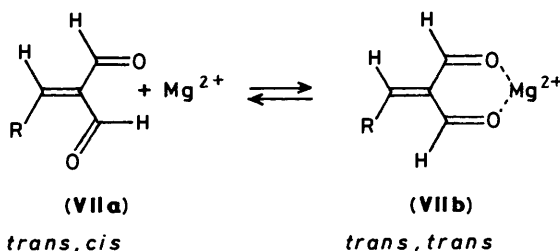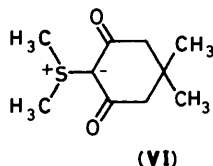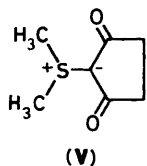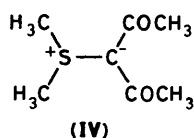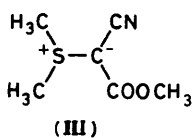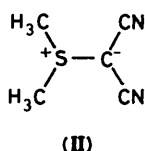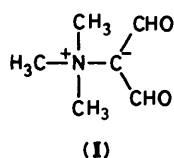
Also the structures of the sulphonium ylides are rather well characterized.[7,10–13] The S–C–C=O group seems to possess significant betaine nature.[10,11] The sulphur has been suggested to adopt a tetrahedral co-ordination,[7] also shown by X-ray diffraction.[13] The binding site of metal cations is shown to be most probably the ylide carbon.[5,6]

In the present work, the complex formation of the compounds with alkali, magnesium, and silver perchlorates and silver tetrafluoroborate was probed by using spin–spin coupling

constants and ^1H and ^{13}C chemical shifts. Concentration and temperature dependencies of the chemical shifts were applied to study the thermodynamics of the complexes. Some complexes were rather easily crystallized out of the solution, and to examine the structures of the crystallized materials, the structure of one complex was solved by X-ray diffraction.

Experimental

Compounds (I)–(VI) were synthesized as described before.[1–3,11,12]

N.M.R. Measurements.—The samples were prepared by weighing accurate amounts of the ylide (*ca.* 0.1×10^{-3} mol) into solvent (500 mm^3) with 1% tetramethylsilane as an internal standard. The spectra were run on JEOL FX-60, JEOL GSX-270, Bruker AM 250, or Tesla BS 497 100 MHz spectrometers. Temperatures were measured by the methanol method.[14] The commercially available hygroscopic metal salts (p.a. purity) were stored in a vacuum desiccator over P_2O_5 and were weighed in a dry box directly into the n.m.r. tube. For accurate measurements of the thermodynamic constants, saturated solutions were prepared from some metal salts and gradually added by a micropipette to the n.m.r. sample in dry conditions. After the measurements the solutions were diluted to a fixed volume and magnesium or silver were titrated with EDTA or KBr.

Data Collection and Processing.—Enraf–Nonius CAD-4 diffractometer, $\omega/2\theta$ scan mode, $2\theta_{max} = 60°$, ω scan speed 1–17° min^{-1}, ω scan width $= 0.50 + 0.34\tan\theta$, graphite monochromatized Mo-K_α radiation, 3 081 independent reflections giving 1 662 with $I > 3\sigma(I)$.

Structure Analysis and Refinement.—The co-ordinates of Cl, Na, and O atoms were determined by direct methods,[15] and C and H atoms from subsequent difference Fourier calculations, Lorenz and polarization corrections, empirical absorption correction,[16] and correction factors: max 1.111 and min 0.871. All non-H atoms anisotropic and H atoms with fixed isotropic temperature factors $B_{eq} = 5.0$ Å^2. Least-squares refinement (with secondary extinction correction: $g = 1.33 \times 10^{-6}$) based on unit weights and F values on a μ-VAX I using the SDP program package.[17] The refinement converged with 181 parameters to $R = 0.036$, $R_w = 0.037$. Residual electron density was 0.33(7) e Å^{-3}.

Results and Discussions

Structure and Complexes of (I) *in Solution.*—The lithium, magnesium, and silver perchlorates induce non-linear chemical shift changes relative to the metal cation concentration. The changes induced with the sodium salts are rather linear. The non-linear changes cannot be explained by intrinsic solvent effects (such as reaction field effect) that should induce nearly linear dependence. Table 1 shows the chemical shifts changes related to metal:ylide molar ratios for (I). In general, if the non-linearity and the magnitude of the induced effects are assumed to be a measure of strength of the complex, $NaClO_4$ forms the weakest complex. Neither is the complex formation with the other reagents very strong (in these solvents), because the complexation seems to be incomplete still in 2:1 metal–ylide molar ratio or even stronger metal solutions. While the changes induced in the formyl–proton shifts are similar for the silver and magnesium salts, the induced CH_3 shifts have a different sign. The behaviour of the $LiClO_4$-induced shifts can be thought as an intermediate of those induced by $Mg(ClO_4)_2$ and $NaClO_4$.

The magnitudes and directions of the induced shifts for the

other compounds were similar. In many cases solid material was crystallized out of the solutions with addition of the metal salt. Because also the behaviour of the chemical shifts of the (II)–(IV) and (V)–(VI) type systems was rather similar, more detailed n.m.r. experiments were carried out only for (I) and (VI). When preparation of stable crystals succeeded for the $NaClO_4$–(I) precipitate, an X-ray diffraction analysis was done for it.

The binding between a metal cation and (I) can take place as in methylenemalonaldehydes,[8,9] that is, simultaneously to both the formyl oxygens (Ia), or between the metal cation and one oxygen for each ylide molecule (Ib), or between the metal cation and the ylide carbon (Ic). Species (Ia) involves a *trans,trans*

(Ia)   (Ib)

(Ic)
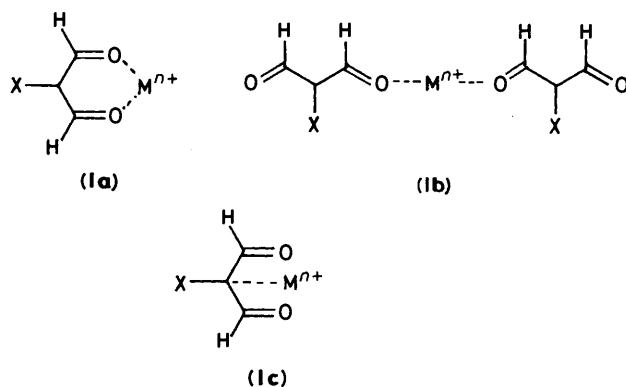
arrangement of the carbonyls and its presence can be probed by the $^3J(^{13}CHO,C^1HO)$ coupling. The value at 298 K in CD_3CN in the absence of a metal cation is 3.00 Hz and is increased only to *ca.* 3.2 (±0.1) Hz (Table 2) in conditions where the complexation is assumed to be rather complete. $^3J(^{13}CHO,C^1-HO)$ and $^3J(^{14}N,C^1HO)$ are insensitive also to solvent, in contrast with the methylenemalonaldehydes,[8] implying that (I) exists in one predominant conformation, in accord with the theoretical calculations.[4] The ^{14}N quadrupolar couplings disturbed accurate determinations of the spectral parameters in the salt solutions. If the observed value of ^3J in neat CD_3CN represents the value of $^3J_{cis}(^{13}CHO,C^1HO)$ (which is relatively large) and if we assume the same $^3J_{trans}/^3J_{cis}$ ratio of 3 as observed for salicylaldehyde,[18] we may conclude that complex (Ia) is formed only to a small extent, if at all.

Almost as many $C=O-M^{n+}$ bonds per M^{n+} as in (Ia) are obtained by structure (Ib), M_mY_m if m is large. Structure (Ib) is observed also in the solid (I)–$NaClO_4$ complex (see later). Structures (Ib, c) do not involve a change of the conformations of the formyl group and have no well known probe. However, the addition of $Mg(ClO_4)_2$ as above increases the value of $^1J(^{13}C^1HO)$ from 165.9 to 176.7 Hz (Table 2). This change is similar to the corresponding shift from 185 to 195 Hz, observed for methylenemalonaldehydes.[7] Because it seems rather improbable that bonding to the ylide carbon would cause so large a positive change in $^1J(^{13}C^1HO)$, we suggest that the oxygen is the predominant bonding site for (I). Although the chemical shifts are less reliable in this type of problem, the metal cation-induced shifts in the carbon chemical shifts of (I) (Table 2) show that the formyl carbon is more influenced by the bonding than the other carbons, in contrast with the sulphonium ylides (for which bonding to ylide carbon is strongly indicated), again supporting structure (Ib).

The presence of the complex (Ic) is claimed for some monocarbonyl-stabilized sulphonium ylides on the basis of the increase of the $C=O$ stretching wavenumber from 1 580 to 1 670 cm^{-1} on complexation with a transition-metal cation (in KBr).[5,6] No shift is observed for the solid (I)–$NaClO_4$ complex,[3] the structure of which is now shown to be of type (Ib).

Table 1. ^{1}H N.m.r. chemical shift changes ($\Delta\delta$), in Hz at 100 MHz, of trimethylammonium diformylmethylide (I) as a function of metal:ylide molar ratio, as measured at 298 K in [^{2}H$_6$]acetone and [^{2}H$_4$]methanol.

	Metal:ylide									
	1.0		2.0		5.0		10.0		saturated	
Salt	CH$_3$	CHO	CH$_3$	CHO	CH$_3$	CHO	CH$_3$	CHO	CH$_3$	CHO
LiClO$_4$[a]	0.1	0.6	0.1	1.3	−0.4	1.7	−2.0	2.2	−4.4	2.9
NaClO$_4$[a]	0.3	0.6	0.3	1.0	0.7	1.9	1.3	2.9	2.0	3.6
NaSCN[a]	0.1	1.3	0.3	2.3	1.8	4.5	4.1	7.8		
Mg(ClO$_4$)$_2$[a]	−4.1	2.7	−6.2	4.3	−7.4	5.3			−9.0	6.4
AgClO$_4$[b]	6.4	5.8	14.2	10.6	16.6	10.3	16.7	11.4		

[a] Measured in [^{2}H$_4$]methanol. [b] Measured in [^{2}H$_6$]acetone.

Table 2. ^{13}C N.m.r. chemical shifts (in ppm) and some coupling constants (Hz) of trimethylammonium diformylmethylide in various solvents.

Solvent	$\delta(CH_3)$	$\delta(C^-)$	$\delta(CHO)$	$^1J(CHO)$	$^3J(CHO,C)$
D$_2$O[a]					3.20
C$_6$D$_6$[a]					3.00
CD$_3$CN[a]	56.0	123.5	180.8	165.9	3.00
Mg(ClO$_4$)$_2$:CD$_3$CN[b]	56.5	125.2	185.2	176.6	3.2
AgClO$_4$:CD$_3$CN[c]	56.0	123.8	181.6	168.3	3.05
[^{2}H$_6$]Acetone[a]	55.7	123.3	180.1	165.0	3.00
AgClO$_4$-[^{2}H$_6$]acetone[d]	55.9	123.6	184.6	174.1	

[a] ca. 5 w/v %, at 298 K. [b] Ylide (0.2 mol dm^{-3}) and Mg(ClO$_4$)$_2$ (0.5 mol dm^{-3}) in CD$_3$CN. [c] Ylide (0.2 mol dm^{-3}) and AgClO$_4$ (0.3 mol dm^{-3}) in CD$_3$CN. [d] Ylide (0.2 mol dm^{-3}) and AgClO$_4$ (5.5 mol dm^{-3}) in CD$_3$CN.

Table 3. Fractional co-ordinates for trimethylammonium diformyl-methylide–NaClO$_4$.

Atom	x	y	z
Cl	0.147 1(1)	0.128 51(3)	0.015 60(7)
Na	0.695 7(2)	0.046 02(6)	0.117 1(1)
O(1)	0.571 9(3)	0.045 8(1)	−0.151 9(2)
O(2)	0.764 7(4)	0.076 6(1)	−0.624 0(2)
O(3)	0.378 6(3)	0.134 8(1)	0.090 1(2)
O(4)	0.116 1(4)	0.068 0(1)	−0.080 9(3)
O(5)	0.079 5(5)	0.190 0(1)	−0.072 5(3)
O(6)	0.015 3(4)	0.121 5(2)	0.125 8(3)
N	0.557 7(4)	0.152 9(1)	−0.408 6(2)
C(1)	0.658 0(4)	0.037 7(1)	−0.260 9(3)
C(2)	0.660 3(4)	0.081 0(1)	−0.386 0(3)
C(3)	0.755 8(4)	0.052 0(2)	−0.499 2(3)
C(4)	0.366 0(6)	0.154 1(2)	−0.543 3(4)
C(5)	0.731 0(7)	0.205 3(2)	−0.433 9(5)
C(6)	0.477 7(8)	0.178 9(2)	−0.275 0(4)
H(1)	0.737(6)	−0.007(2)	−0.264(4)
H(3)	0.821(6)	0.006(2)	−0.467(4)
H(41)	0.264(6)	0.125(2)	−0.499(4)
H(42)	0.300(6)	0.204(2)	−0.556(4)
H(43)	0.431(6)	0.140(2)	−0.636(4)
H(51)	0.757(6)	0.194(2)	−0.529(4)
H(52)	0.667(6)	0.249(2)	−0.446(4)
H(53)	0.866(6)	0.201(2)	−0.347(4)
H(61)	0.593(6)	0.178(2)	−0.196(4)
H(62)	0.412(6)	0.225(2)	−0.310(4)
H(63)	0.342(6)	0.147(2)	−0.275(4)

Figure 1. PLUTO[19] plot of the trimethylammonium diformylmethylide (I) molecule.

The energetics of complex formation is discussed in a later section.

Crystal Structure of the NaClO$_4$–(I) *Complex.—Crystal Data.* C$_6$H$_{11}$ClNaNO$_6$, M = 251.60. Monoclinic, a = 6.131(1), b = 18.889(3), c = 9.095(3) Å, β = 102.97(3), V = 1 026.3(6) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.7017 Å), space group $P2_1/c$ (No. 14), Z = 4, D_x = 1.63 Mg m^{-3}. Colourless prismatic crystals. Crystal dimensions: 0.15 × 0.15 × 0.20 mm, μ(Mo-K_α) = 4.2 cm^{-1}.

The fractional co-ordinates, bond distances, and bond angles for NaClO$_4$–(I) are presented in Tables 3–5. The view of the ylide molecule is shown in Figure 1 and the partial crystal structure of the complex is presented in Figure 2.

The formyl oxygens of (I) in NaClO$_4$–(I) in the crystalline state are *cis,cis* oriented (Figures 1 and 2), differing thus from the diarylmethylenemalonaldehyde lithium and magnesium perchlorate complexes, which show a *trans,trans* conformation.[8] The carbon–carbon bond length in (I) is

Actually, the structure (Ic) is theoretically improbable because it involves an interaction of a cation with a charge localized on the p$_z$ type orbital of the sp^2 hybridized ylide carbon (the formal charge on the basis of CNDO/2 calculations is −0.207). An effective interaction with the electron pair would involve a change of the sp^2 hybridization toward the sp^3 hybridization. Because the change of hybridization would mean losing the hyperconjugative interaction to the nitrogen, it is not probable for cations like Mg^{2+}. The chemical shift changes caused by AgClO$_4$ (Table 2) indicate similar bonding as with Mg(ClO$_4$)$_2$.

Table 4. Bond distances (Å) for trimethylammonium diformylmethylide–NaClO₄.

Cl–O(3)	1.434(2)	N–C(4)	1.496(4)	C(4)–H(43)	1.04(4)
Cl–O(4)	1.428(2)	N–C(5)	1.507(5)	C(5)–H(51)	0.94(4)
Cl–O(5)	1.418(2)	N–C(6)	1.492(5)	C(5)–H(52)	0.91(4)
Cl–O(6)	1.428(3)	C(1)–C(2)	1.404(4)	C(5)–H(53)	1.01(3)
Na–O(1)	2.394(2)	C(1)–H(1)	0.97(4)	C(6)–H(61)	0.89(3)
Na–O(3)	2.537(2)	C(2)–C(3)	1.405(4)	C(6)–H(62)	0.97(4)
Na–O(1)	2.457(2)	O(1)–C(1)	1.233(3)	C(3)–H(3)	0.98(4)
Na–O(2)	2.368(2)	C(6)–H(63)	1.03(4)	O(2)–C(3)	1.239(3)
Na–O(4)	2.450(3)	C(4)–H(41)	0.99(4)	N–C(2)	1.492(3)
Na–O(6)	2.410(3)	Na–Na	3.320(1)	C(4)–H(42)	1.01(4)

Table 5. Bond angles (°) for trimethylammonium diformylmethylide–NaClO₄.

O(3)–Cl–O(4)	109.8(1)	C(5)–N–C(6)	106.3(3)	H(41)–C(4)–H(43)	125.0(3)
O(3)–Cl–O(5)	109.4(2)	O(1)–C(1)–C(2)	131.5(3)	H(42)–C(4)–H(43)	112.0(3)
O(3)–Cl–O(6)	109.4(2)	O(1)–C(1)–H(1)	116.0(2)	N–C(5)–H(51)	105.0(2)
O(4)–Cl–O(5)	109.0(1)	C(2)–C(1)–H(1)	112.0(2)	N–C(5)–H(52)	108.0(2)
O(4)–Cl–O(6)	109.8(2)	N–C(2)–C(1)	124.2(2)	N–C(5)–H(53)	108.0(2)
O(5)–Cl–O(6)	109.4(2)	N–C(2)–C(3)	119.1(2)	H(51)–C(5)–H(52)	105.0(3)
O(1)–Na–O(3)	90.90(7)	C(1)–C(2)–C(3)	116.6(2)	H(51)–C(5)–H(53)	115.0(3)
O(1)–Na–O(1)	93.62(7)	O(1)–Na–O(2)	164.04(9)	O(1)–Na–O(4)	85.06(8)
O(1)–Na–O(6)	95.93(8)	O(3)–Na–O(4)	157.37(8)	O(3)–Na–O(6)	102.23(9)
Na–O(1)–C(1)	136.7(2)	O(2)–C(3)–C(2)	129.6(3)	H(52)–C(5)–H(53)	115.0(3)
Cl–O(3)–Na	130.3(2)	O(2)–C(3)–H(3)	121.0(2)	N–C(6)–H(61)	108.0(2)
C(2)–N–C(4)	110.9(3)	C(2)–C(3)–H(3)	110.0(2)	N–C(6)–H(62)	102.0(2)
C(2)–N–C(5)	109.2(2)	N–C(4)–H(41)	96.0(2)	N–C(6)–H(63)	103.0(2)
C(2)–N–C(6)	113.1(3)	N–C(4)–H(42)	109.0(2)	H(61)–C(6)–H(62)	118.0(3)
C(4)–N–C(5)	108.5(2)	N–C(4)–H(43)	107.0(2)	H(61)–C(6)–H(63)	119.0(3)
C(4)–N–C(6)	108.7(3)	H(41)–C(4)–H(42)	107.0(3)	H(62)–C(6)–H(63)	104.0(3)
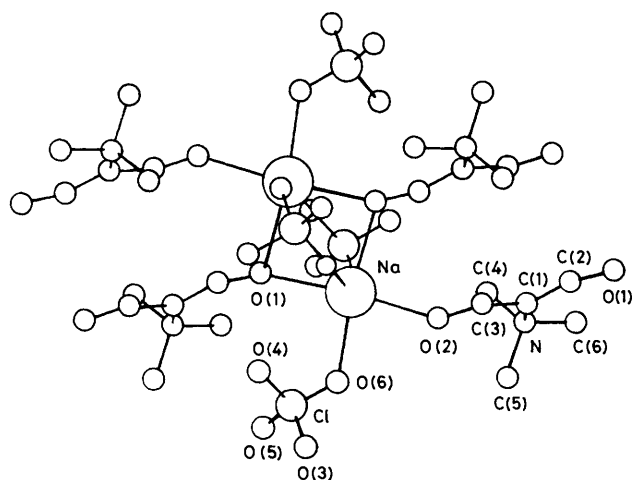
Figure 2. A partial view [20] of packing for trimethylammonium diformyl-methylide–NaClO₄ complex.

1.404(4) Å, which is shorter than a typical single sp²–sp² carbon bond (1.46 Å [21]), showing thus clear double-bond character. The bond lengths between nitrogen and methyl carbons, 1.496(4), 1.507(5), and 1.492(5) Å and nitrogen and ylide carbon, 1.492(3) Å, are greater than 1.47 Å,[21] which is the standard value for an sp³-hybridized carbon–nitrogen single bond. The values are in quite good agreement with values calculated by the CNDO/2 method, 1.40 Å for C–C and 1.45 Å for C–N bond in ylide (I)[4] and with the X-ray values of 1.34 and 1.48 Å for related structures.[22] The Na–O=C and Na⁺–OClO₃ bond lengths are nearly equal and suggest the Na⁺–(I) interaction is a pure ion–dipole interaction. Thus the structure of the ylide (I) in the crystal state is probably a reasonable model for that of the pure ylide.
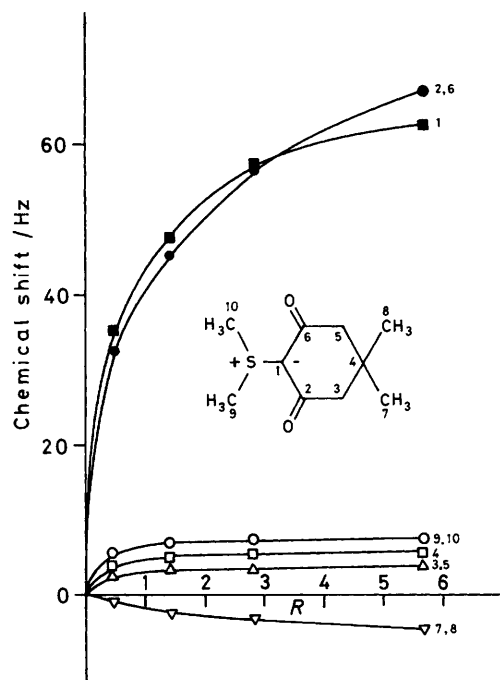
Figure 3. ¹³C N.m.r. chemical shift changes (Hz) for ylide (VI) as a function of AgBF₄:ylide molar ratio (R) in acetone.

Complex Formation of (VI).—Figure 3 shows the ¹³C n.m.r. chemical shift changes as a function of AgBF₄:ylide (VI). The most interesting point is that both the carbonyl and the ylide carbons are equally sensitive to the cation. In comparison with the ylide (I), for which only the formyl carbon experienced a remarkable shift, and for which the other data support bonding

Table 6. Complex formation energetics for some ammonium and sulphonium ylides.

| Ylide | M | Solvent | Thermodynamic parameters[a] | | | Spectral parameters[a] | | | |
			$\Delta G(300\ K)/$ kJ mol^{-1}	ΔH/J K^{-1} mol^{-1}	ΔS/kJ mol^{-1}	$\delta_1(MY)^b$	$\delta_2(MY)^c$	$d\delta/dM$	RRMS/n^d
(I)	AgBF$_4$	Acetone	-10			4.7	2.8	0	0.8/5
(II)	Mg(ClO$_4$)$_2$	Acetone	-10			2.5		0	1.9/9
(III)	AgBF$_4$	Acetone	-10			6.7	9.4	0	1.5/5
(III)	AgClO$_4$	Acetone	-10			7.1	10.1	0	1.8/5
(III)	Mg(ClO$_4$)$_2$	CD$_3$CN	-10			6.7	3.5	0	0.3/5
(IV)	AgBF$_4$	Acetone	$-9.2(26)$			4.9(3)	14.0(4)	1.4(9)	0.7/10
(IV)	AgClO$_4$	Acetone	$-9.9(22)$			5.0(3)	13.1(4)	2.2(9)	0.7/10
(V)	AgBF$_4$	Acetone	$-7.1(25)$			8.0(7)	20.5(1)	$-2.8(16)$	0.8/10
(VI)	AgBF$_4$	Acetone	$-9.1(3)$	$-34.1(5)$	85.6(20)	11.1(2)	21.2(3)	$-5.4(\ )$	0.8/10

[a] The numbers in parentheses give the standard deviation in the last significant number. If not given the parameter was not optimized. [b] The high-field chemical shift. [c] The low-field chemical shift. [d] RRMS = residual root mean square, n = No. of data points.
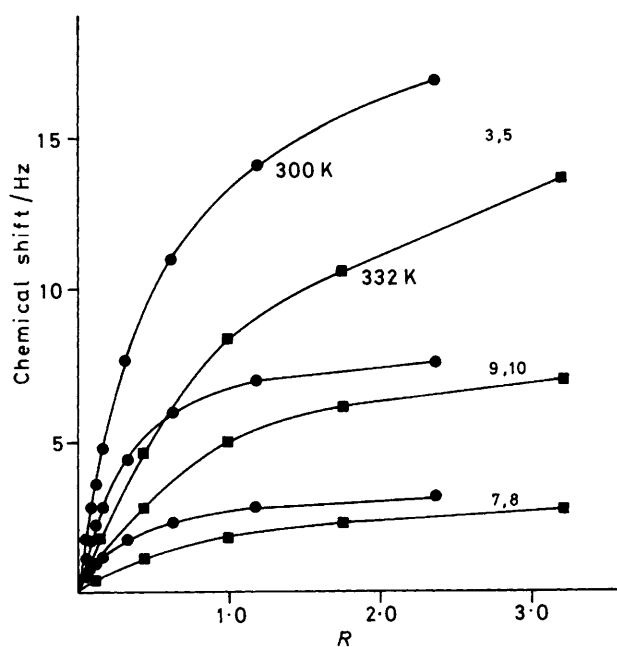

Figure 4. ^{1}H N.m.r. chemical shift changes (Hz) for ylide (VI) as a function of AgBF$_4$:ylide molar ratio (R) in acetone at 300 (●) and 332 K (■).

Figure 5. ^{1}H N.m.r. chemical shift changes (Hz) for ylides (IV) and (V) as a function of AgBF$_4$:ylide molar ratio (R).

to the oxygen, this suggests now that also the bonding found in (Ic) would be possible. Similar shifts are also obtained by Mg(ClO$_4$)$_2$.

Complex Formation Energetics of (I) *and* (VI).—A rough picture of the complex formation energetics for (I) and (VI) was obtained by fitting the concentration and temperature dependence of the ^{1}H chemical shifts, assuming only a one-step complexation equilibrium [equation (1)] and that the other

$$Y + M \rightleftharpoons YM \qquad (1)$$

possible complexes Y$_n$M$_m$, if any, have the same chemical shifts as YM. If the bonding in the complexes is similar, the assumption is reasonable. The presence of the other complexes may be seen from the value of the entropy component of the complex-formation free energy. In any case, our calculations imply that no more than one equilibrium constant is obtained accurately on the basis of the chemical shifts, which also depend on the various intrinsic effects. To account for the intrinsic solvent effects we included the term $k_1[M_{tot}]$ into the statistical average
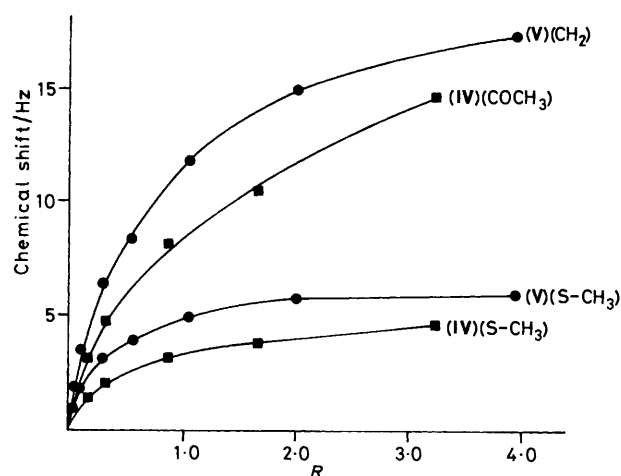
of the chemical shift [equation (2) where $v(Y)$ and $v(YM)$ are

$$v_{obs} = v(Y)X(Y) + v(YM)X(YM) + k_1[M_{tot}] \qquad (2)$$

the chemical shifts (in Hz) of the free ylide and the complex and X(Y) and X(YM) are their mole fractions, respectively]. The data fit was done by the program EQUILA.[23]

The fit was carried out or attempted for each of compounds (I)–(VI), the results being given in Table 6. In some cases the fit failed to give sensible values of some parameters; in those cases some appropriate values were used. To summarize, the complex-formation free energies do not depend markedly on the stabilizing group and vary in range -5 to -10 kJ mol^{-1} at 300 K.

The temperature dependence of chemical shifts shown in Figure 4 also gave an estimate of the entropy, ΔS° 85 $\pm$ 2 J K^{-1} mol^{-1}. The entropy difference can be seen directly from the temperature dependence of the experimental data. At higher temperatures the induced shifts are smaller, meaning a looser complexation than at lower temperatures. Inclusion of the ^{13}C n.m.r. data into the optimization run did not alter the result obtained by the proton data alone. The relatively large value of ΔS supports a highly ordered structure, such as (Ib). Corresponding analysis for (I) failed to give an unambiguous value of ΔS, obviously due to the rather small induced shifts and the problems arising from broad lines induced by nitrogen quadrupole coupling and the intrinsic solvent dependence of the shifts.

For comparison, in Figure 5 is shown the chemical shift behaviour of the ^1H n.m.r. chemical shifts of (**IV**) and (**V**).

Conclusions.—The dicarbonyl-stabilized ammonium and sulphonium ylides have a clear tendency to form complexes with alkali, magnesium, and silver salts. Some complexes are easily crystallized out of the solution. In the case of the ammonium ylides (**I**) the predominant structure is probably that in which the cation is bound to the carbonyl oxygen. For the sulphonium ylides such as (**VI**) bonding to the ylide carbon is preferred. Obvious explanations are the different character of S^+-C^- and N^+-C^- bonds and the flexibility[24] and the bigger negative charge [-0.225 for (**VI**)[11] *versus* -0.207 for (**I**)[4] computed by the CNDO/2 method] of the ylide carbon region in the sulphonium ylides. The double bond character of the S^+-C^- bond arises from p–d interactions, stabilized by δ electron back-donation,[11] and is thus more flexible than the sp^2 structure of the ammonium ylide carbon, which may be stabilized by a hyperconjugation-type interaction of the π-electrons with the methyl carbons.

The complex formation of both the ammonium and sulphonium ylides is relatively sensitive to temperature; the observed reaction entropy, -85 J K^{-1} mol^{-1} is large for example in comparison with -33 J K^{-1} mol^{-1} found for Cs$^+$ and dibenzo-24-crown-8 in CD$_3$CN.[26]

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