The Carbonyl Group Frequency.   Part VI.[1]   Alkyl Carbonates

By **J. Sydney Byrne, Paul F. Jackson,** and **Keith J. Morgan,*** Department of Chemistry, University of Lancaster, Lancaster LA1 4YA

Calculations for a simplified model suggest that the similarity in carbonyl frequencies for carbonate and carboxylate esters arises from compensating changes in $k_{C=O}$ and other vibration parameters.   A revised assignment for the in-plane skeletal bands of dimethyl carbonate is proposed.   The carbonyl frequencies of di-methyl, -ethyl, and -isopropyl carbonate show regular substituent and solvent effects; variation in the values for di-t-butyl carbonate accords with the *s-cis–s-trans*-form (3) being more stable in polar solvents.   The high group frequency and solvent sensitivity shown by propylene carbonate is attributed to the effects of electronic repulsions in the *s-trans–s-trans*-structure.

REPLACEMENT of an alkyl group in a ketone by an alkoxy-group causes spectroscopic perturbations which have been well documented for change to a carboxylic ester.[2]   There have been fewer reports of the effects accompanying further change to a carbonic ester. Complete vibrational assignments have been reported for dimethyl carbonate[3] and ethylene carbonate;[4] correlations with structural effects have been reported for dialkyl carbonates;[5] and solvent effects have been studied for ethylene carbonate.[6]   The effects of solvents and structure on carbonyl group frequencies for simple and cyclic dialkyl carbonates are now reported.

EXPERIMENTAL

Dimethyl, diethyl, and ethylene carbonate were commercial samples purified by distillation. Conventional methods were used to prepare di-isopropyl carbonate,[7] b.p. 144°; di-t-butyl carbonate,[8] b.p. 154°; and 1,3-propylene carbonate,[9] b.p. 123° at 1 mmHg.   In each case examination by g.l.c. showed that the product was better than 98% pure; examination by n.m.r. spectroscopy gave spectra in accord with expectation.

Solution spectra were measured by using 0.1 mm cells for *ca.* 0.1M solutions in acetonitrile, dimethyl sulphoxide, dioxan, and nitromethane; for other solvents 1.0 mm cells with *ca.* 0.01M solutions were used.   Vapours were examined in a 10 cm cell at pressures of 5—20 mmHg.   Spectra were recorded on a Perkin-Elmer model 225 spectrometer with dry air flushing.   Calibration was by interpolation from external water vapour bands;[10] quoted values are believed to be accurate to better than ± 1 cm^{-1}.

Vibrational frequencies were calculated for conventional F and G matrices[11] for a tetra-atomic model using the following parameters: $r_{C=O}$ 1.22, r_{C-O} 1.37 Å, $k_{C=O}$ 9.77, k_{C-O} 4.8, $h_{OC=O}$ 1.0, h_{OCO} 0.7, $f_{C-O,C-O}$ 1.0, $f_{C-O,OC=O}$ 0.16 mdyn Å^{-1}.

[1] Part V, J. S. Byrne, P. F. Jackson, K. J. Morgan, and N. Unwin, *J.C.S. Perkin II*, 1973, 845.
[2] *E.g.* K. J. Morgan and N. Unwin, *J. Chem. Soc. (B)*, 1968, 880.
[3] B. Collingwood, H. Lee, and J. K. Wilmshurst, *Austral. J. Chem.*, 1966, **19**, 1637.
[4] C. L. Angell, *Trans. Faraday Soc.*, 1956 **52**, 1178; R. Mecke, R. Mecke, and A. Lüttringhaus, *Chem. Ber.*, 1957, **90**, 975; J. R. Durig, G. L. Coulter, and D. W. Wertz, *J. Mol. Spectroscopy*, 1968, **27**, 285; J. R. Durig, J. W. Clark, and J. M. Caspar, *J. Mol. Structure*, 1970, **5**, 67; B. Fortunato, P. Mirone, and G. Fini, *Spectrochim. Acta*, 1971, **27**, 1917.
[5] A. R. Katritzky, J. M. Lagowski, and J. A. T. Beard, *Spectrochim. Acta*, 1960, **16**, 964; J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 1957, 618; H. Minato, *Bull. Chem. Soc. Japan*, 1963, **36**, 1020.
[6] L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, 1959, **55**, 14; J. F. Bertran, L. Ballester, L. Dobrihalova, N. Sanchez, and R. Arrieta, *Spectrochim. Acta*, 1968, **24A**, 1765.

RESULTS

Carbonyl stretching frequencies for some cyclic and acylic carbonate esters are in Table 1.   The bands for dimethyl and diethyl carbonate as vapours show rotational fine structure and the quoted values refer to the band centres. The band for ethylene carbonate as vapour or solution in non-polar solvent is complex;[4] in dioxan and more polar solvents the carbonyl region contains two well resolved and symmetrical bands.   Band envelopes for other esters become broader and less symmetrical in polar solvents.

In-plane vibrational frequencies calculated for a simple tetra-atomic model (1) are in Table 2.   This model is arbitrary in that the C–O stretching constant was set at the value used previously[12] for methyl acetate (4.8 mdyn
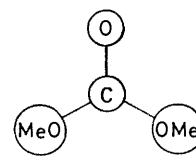
(I)
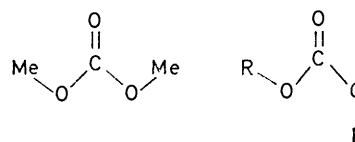
(II)   (III)

Å^{-1}); the other constants were adjusted to obtain satisfactory agreement with observation (see Discussion section). The approximate potential energy distribution (p.e.d.) for the carbonyl vibration is not significantly modified by small changes in k_{C-O}.

DISCUSSION

The local symmetry of the carbonate residue is C_{2v}. For dimethyl carbonate physical measurements[3,13]

[7] K. W. F. Kohlrauch and R. Sabathy, *Monatsh.*, 1939, **72**, 303.
[8] A. R. Choppin and J. W. Rodgers, *J. Amer. Chem. Soc.*, 1948, **70**, 2967.
[9] L. A. Pohoryles and S. Sarel, *Compt. rend.*, 1957, **245**, 2321.
[10] I.U.P.A.C. Tables of Wavelengths for the Calibration of Infrared Spectrometers, Butterworths, London, 1961.
[11] E. B. Wilson, J. C. Decius, and P. C. Cross, ' Molecular Vibrations,' McGraw-Hill, New York, 1955.
[12] A. J. Collings, P. F. Jackson, and K. J. Morgan, *J. Chem. Soc. (B)*, 1970, 581.
[13] R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 1383; G. Thomson, *ibid.*, 1939, 1118; G. F. Longster and E. E. Walker, *Trans. Faraday Soc.*, 1953, **49**, 228; J. M. O'Gorman, W. Shand, and V. Schomaker, *J. Amer. Chem. Soc.*, 1950, **72**, 4222.

indicate that this symmetry applies to the full heavy atom skeleton with the methoxy-groups adopting a s-*cis*–s-*cis* configuration (2). For bulkier carbonates an alternative s-*cis*–s-*trans* configuration (3) may be adopted [14] and in cyclic carbonates the molecule has necessarily an s-*trans*–s-*trans* arrangement.

ment also removes an apparent anomaly [17] in the value for the symmetrical bending vibration.

The effect of introducing a second oxygen substituent into the model is to reduce the carbonyl force constant to a value (9.77 mdyn $Å^{-1}$) lower than is found [12,18] for either acetone or methyl acetate (10.42, 10.35 mdyn

TABLE 1
Carbonyl group frequencies (cm^{-1}) of dialkyl carbonates

	$(MeO)_2CO$	$(EtO)_2CO$	$(Pr^iO)_2CO$	$(Bu^tO_2)CO$	$C_2H_4O_2CO$		$C_3H_6O_2CO$
Vapour	1 774	1 763.5	1 752	1 748	1 862.5		1 814
Solvent							
C_6H_{14}	1 760.5	1 750	1 742	1 740.5	1 842		1 790
C_6H_{12}	1 760	1 750	1 742.5	1 740.5	1 842		1 788
CCl_4	1 756.5	1 745.5	1 737.5	1 739	1 831	1 768	1 776
CS_2	1 754	1 743.5	1 736	1 736	1 828	1 765	1 772
Dioxan	1 755	1 744	1 737	1 737	1 813	1 774.5	1 763
MeCN	1 755.5	1 745	1 736	1 735	1 807.5	1 777.5	1 750.5
$MeNO_2$	1 755	1 744	1 735	1 735.5	1 807	1 778	1 749
CH_2Cl_2	1 753	1 741	1 733	1 735	1 810.5	1 776.5	1 753
$CHCl_3$	1 751	1 740	1 733	1 734	1 811.5	1 779	1 753
$CHBr_3$	1 747.5	1 737	1 729	1 732	1 808	1 776.5	1 748.5
Me_2SO	1 751	1 740.5	1 731	1 731	1 802	1 774.5	1 742
m [a]	0.67	0.68	0.61	0.46	1.76		2.08

[a] Gradient of $\nu = m\nu_{MCOAC} + d$

TABLE 2
Calculated frequencies (cm^{-1}) and potential energy distribution for in-plane skeletal vibrations of dimethyl carbonate

	Frequency	Potential energy distribution					Approximate description
		S_1	S_2	S_3	S_4	S_5	
A_1	1 775	71.5	15.1	13.5			C=O stretch
	851	24.8	70.6	4.5			O–C–O symm. stretch
	585	4.8	15.3	79.7			O–C–O bend
B_1	1 297				57.7	42.3	O–C–O asymm. stretch
	628				40.9	59.1	C=O i.p. wag

The in-plane vibrations of the carbonate residue can be estimated by using the simple tetra-atomic oscillator which has been applied to other carbonyl systems.[1,12] With k_{C-O} set at 4.8 mdyn $Å^{-1}$ the frequency previously assigned [3] to the symmetric O–C–O stretching vibration for dimethyl carbonate could only be generated by the use of large bending and interaction constants (*i.e.*

TABLE 3
Bands in the i.r. spectra of dimethyl carbonate

Approximate description	Frequency (cm^{-1}) [a]	Frequency (cm^{-1}) [b]
C=O stretch	1 774	1 774
O–C–O symm. stretch	1 116	857
O–C–O bend	857	585
O–C–O asymm. stretch	1 299	1 299
C=O i.p. wag	634	634

[a] Ref. 3. [b] Proposed assignment. Polarisations are similar for the Raman bands at 857 and 1 116 cm^{-1}; polarisation of the Raman band at 576 cm^{-1} was indeterminate.

$h_{OC=O'}$ $f_{C-O,OC=O'}$ $f_{C-O, C-O}$ *ca.* 3—4 mdyn $Å^{-1}$). Since comparison with carbonyl fluoride [15] and other O–C–O systems [16] suggests the assigned frequency is high we prefer an alternative assignment (Table 3); this assign-

$Å^{-1}$). These values are in accord with the larger conjugated system of carbonates and are supported by simple MO calculations of carbonyl bond order.[19] The reduction in carbonyl force constant would alone reduce the calculated group frequency by *ca.* 45 cm^{-1}. The frequency for methyl carbonate remains close to that for methyl acetate because of compensating changes due to other elements shown by the p.e.d. to contribute to the group frequency *viz.* O–C–O symm. stretch, O–C–O symm. bend, and the increased values for interaction constants.

The effects of variation in alkyl substituents in ketones,[20] aldehydes,[18] and esters [2] give carbonyl group frequencies in the sequence Me > Et > Pr^i > Bu^t. The same sequence is found for carbonates as vapours but in solvents more polar than cyclohexane the sequence becomes Me > Et > Bu^t > Pr^i. A linear relationship between ν_{CO} and σ^* for di-methyl, -ethyl and -isopropyl carbonates suggests that they have a common s-*cis*–s-*cis*-configuration. Oki and Nakanishi [14] have suggested that t-butyl carbonates adopt the s-*cis*–s-*trans*-configuration (3) and that the corresponding carbonyl

[14] M. Oki and H. Nakanishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 3419.
[15] J. Overend and J. R. Scherer, *J. Chem. Phys.*, 1960, **32**, 1296.
[16] E. D. Bergmann and S. Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161; W. J. Potts and R. N. Nyquist, *Spectrochim. Acta*, 1961, **17**, 679.
[17] H. V. Gründler and E. Steger, *Z. Chem.*, 1972, **12**, 351.
[18] J. S. Byrne, P. F. Jackson, and K. J. Morgan, *J.C.S. Perkin II*, 1972, 1291.
[19] Y. Ono and Y. Ueda, *Chem. and Pharm. Bull.* (*Japan*), 1970, **18**, 2013.
[20] K. J. Morgan and N. Unwin, *J. Chem. Soc.* (*B*), 1967, 1336.

frequency is higher. It is evident from the results for 1,3-propylene carbonate that an s-*trans*–s-*trans* configuration gives a high carbonyl frequency. An s-*cis*–s-*trans*-configuration has also been suggested[14] for di-isopropyl carbonate. Evidence for this is inferred from graphical resolution of the carbonyl band into a weak low frequency and a strong high frequency band. While the evidence is analogous to part of that found for di-t-butyl carbonate it must be interpreted with caution since the carbonyl band for 1,3-propylene carbonate is similarly asymmetric.

The high carbonyl frequencies of the cyclic carbonates are of interest in relation to those of other cyclic carbonyl compounds. Variation of the carbonyl frequency with ring size can largely be attributed directly to variation in the valency angle.[21] Thus by maintaining constant all the parameters except the valency angle, the calculated values for the carbonyl frequency of a simple tetra-atomic model for acetone[18] reproduce the effects of variation in ring size (Table 4). This is confirmed by

TABLE 4

Effects of bond angle on calculated carbonyl frequencies

Angle (°)	60	90	108	120
Calculated ^{a} frequency (cm^{-1})	1 843	1 793	1 759	1 738
Observed ^{b} frequency (cm^{-1})	1 853 ^{c}	1 816	1 769	1 734

^{a} For tetra-atomic model.[18] ^{b} Values for corresponding cyclic ketones as vapours. ^{c} Estimated from value for solution in methylene chloride (N. J. Turro and W. B. Hammond, *Tetrahedron*, 1968, **24**, 6017) by using the expression which applies to other cyclic ketones: $v_{CH_2Cl_2} = 0.903\ v_{vap} + 139.4\ cm^{-1}$.

studies of hydrogen bonding[22] which indicate that only small changes in polarity, and hence in k_{CO} accompany changes in ring size.*

While the higher frequency for ethylene carbonate follows the normal pattern, the high frequency for 1,3-propylene carbonate is unusual in a six-membered ring compound. It is generally accepted[23] that in solution unstrained six-membered ring compounds have carbonyl frequencies similar to those for their open chain analogues; the similarity is maintained for ketones as vapours (cyclohexanone v_{CO} 1 733 cm^{-1}, pentan-3-one, 1 737 cm^{-1}) but the values for esters (δ-valerolactone, 1 777 cm^{-1}; ethyl propionate, 1 760 cm^{-1}) and carbonates (Table 1) diverge. It is unlikely that the high frequency for propylene carbonate can be ascribed to an increased carbonyl force constant: the compound is more basic to proton donors than diethyl carbonate and ^{13}C n.m.r. spectroscopy[24] provides no evidence of any significant change in hybridisation. Calculation suggests that the high carbonyl frequency could arise from increasing the interaction constant $f_{C-O,C-O}$ to *ca.* 2.5 mdyn Å^{-1} but there is no evident justification for such a high value. Alternatively a change in O–C–O bond angle as a result of lone pair repulsions between ether and carbonyl oxygen atoms could raise the carbonyl frequency. Such repulsions, which would have an effect opposite to those in diethyl carbonate, are those normally encountered in s-*cis*-carboxylic systems.[25] It is possible that a similar effect is present in δ-valerolactone.

The effect of solvent on the carbonyl frequencies of carbonate esters is to displace them to lower values. For strain-free acyclic compounds the displacements are regular and satisfy the equation[20] $v_{soln} = nv_{vap} + d$; the cyclic derivatives show substantially greater displacements in polar solvents. This effect is also evident from the modified Bellamy plot,[26] $v_{carbonate} = mv_{ref} + c$ by using methyl acetate as the reference compound. For s-*cis*–s-*cis*-esters the gradient, *m*, has a value 0.6—0.7 but for the bulkier s-*cis*–s-*trans*-di-t-butyl carbonate this falls to 0.46. Conversely for cyclic esters there is a high sensitivity to solvation. As with cyclic ketones, some part of this may be attributed to lower steric hindrance but the higher values for cyclic carbonates and lactones (β-propiolactone, 1.6; γ-butyrolactone, 1.5; δ-valerolactone, 1.6; ϵ-caprolactone, 1.4; *cf.* cyclohexanone, 0.92) suggest that part may also be due to relief of electronic repulsions.

---

* For a heavy atom model with k_{CO} 4.0 analysis suggests a small increase for cyclobutanone (k_{CO} 10.67) with respect to acetone (k_{CO} 10.42).

[21] R. C. Lord and F. A. Miller, *Applied Spectroscopy*, 1956, **10**, 115; J. I. Brauman and V. W. Laurie, *Tetrahedron*, 1968, **24**, 2595.

[22] L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, 1963, **19**, 1831.

[23] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Methuen, London, 1954.

[24] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley, New York, 1972.

[25] N. L. Owen and N. Sheppard, *Proc. Chem. Soc.*, 1963, 264.

[26] L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.