Conformations and Barriers to Inversion of Some Cyclic Seven-membered α-Diketones. A Study by Dynamic Nuclear Magnetic Resonance Spectroscopy and Molecular Mechanics Calculations

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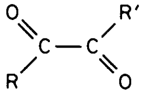
The dynamic stereochemistry of some seven-membered α-diketones have been studied by ^{1}H n.m.r. spectroscopy and by molecular mechanics calculations. A force-field for α-dicarbonyl compounds has been developed. The cyclic α-diketones studied preferably adopt a distorted chair conformation with C_1 symmetry or a C_2 symmetric twist-boat conformation with a carbonyl–carbonyl dihedral angle of 87—102°. The inversion of the seven-membered ring system was interpreted in terms of a passage of the two carbonyl units in a planar *s-cis* conformation. The inversion barriers were found to be 8.6—11.3 kcal mol^{-1} with negligible entropy of activation. Molecular mechanics calculations indicate that the electrostatic contribution to the inversion barrier is 42—52% of the total barrier heights.

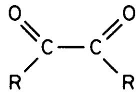
In α-dicarbonyl compounds, the dicarbonyl unit may exist in two planar conformations, *s-cis* and *s-trans*, both stabilized by π-conjugation. Electrostatic repulsion between the carbonyl oxygens and repulsive steric interactions between the substituents R and R′ should strongly disfavour the *s-cis* conformation. In acyclic aliphatic α-dicarbonyl compounds the *s-cis* conformation has only been observed for glyoxal,[1] the simplest member of this class of molecules (R = R′ = H). From the temperature dependence of the electronic spectrum of glyoxal an energy difference of 3.2 kcal mol^{-1} between the *s-cis* and *s-trans* conformations in favour of the latter was determined.[2] For methyl glyoxal[3] (R = H, R′ = CH_3) and biacetyl[4,5] (R = R′ = CH_3) only the *s-trans* conformation has been detected.

Much interest has been paid to the torsional potential and barrier to rotation around the carbonyl–carbonyl bond in simple α-dicarbonyl compounds. The great majority of the investigations, however, has exclusively had glyoxal as their object. A torsional potential function of glyoxal based on i.r. data and microwave intensities gives a rotational barrier of 5.06 kcal mol^{-1} at a dihedral angle of *ca.* 77° (*s-cis* = 0°).[6]

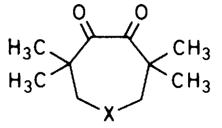
With the exception of the extensively studied glyoxal molecule, very few studies on the dynamic stereochemistry of aliphatic α-dicarbonyl compounds have been published. A Fourier analysis of the gas-phase dipole moments of biacetyl at different temperatures resulted in a rotational barrier for this compound of 7.6 kcal mol^{-1}, with the *s-cis* structure as the transition state.[7] Further analysis of these data in combination with simple empirical calculations of non-bonded interactions gave a potential energy function with a maximum at a dihedral angle of *ca.* 20°, 7.9 kcal mol^{-1} above the energy of the *s-trans* conformation. No significant barrier to rotation from the *s-cis* conformation was found. These studies on biacetyl, however, suffer from the use of a rigid *s-trans* geometry in the calculations of non-bonded interactions and the conclusions, especially for the *s-cis* region, are therefore less reliable. Theoretical calculations on the conformational properties of α-diketones give widely different results depending on the calculational method used and/or the geometries assumed. MINDO/3 calculations on biacetyl using optimized geometries give an energy minimum at a dihedral angle of 105° and energy maxima for the *s-cis* and *s-trans* conformations, inconsistent with experimental data.[8] *Ab initio* calculations (STO-4G) using MINDO/3 geometries give energy minima for *s-cis* and *s-trans* with the *s-trans* conformation at 1.56 kcal mol^{-1} lower energy and with a low energy barrier to rotation, 2.53 kcal mol^{-1}, at a dihedral angle of 83°. Using the rigid rotor approach (*s-trans* geometry) STO-4G calculations give an energy difference between *s-trans* and *s-cis* of 4.42 kcal mol^{-1} in favour of the former. The rotational barrier is calculated to be 4.87 kcal mol^{-1} at a dihedral angle of 68°.[8] The potential-energy function is thus calculated to be very shallow between 68 and 0°. A survey of the available investigations shows that, with the exception of glyoxal, reliable data on the dynamic stereochemistry of aliphatic α-dicarbonyl compounds are very scarce and that the properties of the *s-cis* conformation are largely unknown.



s-trans



s-cis

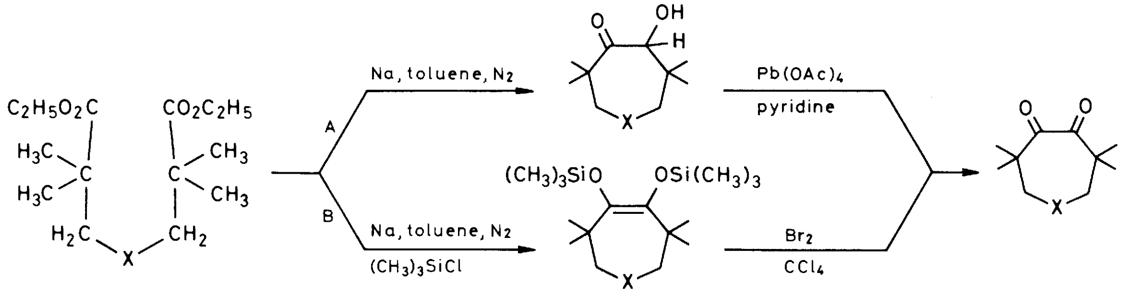


(I) X = CH_2
(II) X = O
(III) X = S
(IV) X = NCH_3
(V) X = $NC(CH_3)_3$

The present work was undertaken to obtain information on the changes in steric and electrostatic interactions with changes in the carbonyl–carbonyl dihedral angle in α-diketones. For this purpose the cyclic α-diketones (I)—(V) have been studied.

After the present work was completed a variable-temperature ^{13}C n.m.r. investigation of (I) and its five-, six-, and eight-membered homologues was reported.[9] The inversion barrier was found to increase with increasing ring size, reflecting an increase of the intercarbonyl dihedral angle in the ground state. For (I) the angle was predicted to be 82°.

A study of the u.v. spectra of (I) and some of its analogues with different ring sizes indicates that the carbonyl–carbonyl dihedral angle in (I) is 90—110°.[12] The inversion of the seven-membered ring system should involve a passage of the two carbonyl groups in a planar or close-to-planar *s-cis* transition



Scheme 1.

state, and the inversion barrier should reflect the electrostatic and steric interactions in this conformation. In the present work the inversion process was studied by dynamic ^1H n.m.r. spectroscopy. The geminal methyl groups in (I)—(V) prevent enolization and also provide n.m.r. signals whose temperature-dependent bandshape could be conveniently used to evaluate rate constants for the inversion process. The substituents X in compounds (II)—(V) were introduced mainly to obtain geometrical variation of the ring system. As a bonus two isolated methylene groups are created whose n.m.r. signals may be used to characterize the inversion process. To aid in the interpretation of the n.m.r. spectra and the observed inversion barriers, geometries and conformational energies were calculated by the molecular mechanics method. For this purpose a force-field for α-dicarbonyl compounds has been developed.

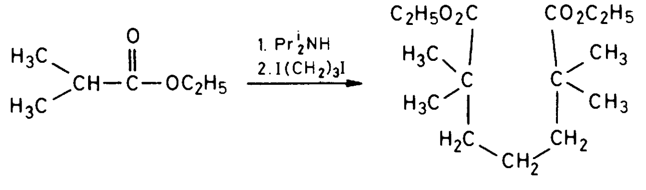
Experimental and Computational

Materials.—The compounds in this work were prepared by the acyloin condensation of the corresponding acyclic diesters and subsequent oxidation of the acyloins or disiloxenes, according to the methods described by Johnson *et al.*[10] (Scheme 1).

Compounds (III)—(V) were prepared according to route A and (I) and (II) according to B. The final products were purified by thin-layer chromatography. The diesters with X = S, NCH_3, and $NC(CH_3)_3$ were obtained as described by de Groot and Wynberg [11] and Johnson *et al.*[10] New routes to prepare the diesters with X = CH_2 and O were developed. A synthesis of diethyl 2,2,6,6-tetramethylpimelate from phenyl isopropyl ketone and 1,3-dibromopropane has been described,[12,13] but we found that the reaction between the anion of ethyl α-isobutyrate and 1,3-di-iodopropane afforded the diester in a more convenient way (Scheme 2).

The method used by Johnson *et al.*[10] to prepare the diester with X = O involves the well known cancerogenous compound bischloromethyl ether. To avoid using this compound we prepared the diester *via* the Williamson ether synthesis. The yield was, however, poor.

Diethyl 2,2,6,6-Tetramethylpimelate.—To a solution of 0.25 mol (25.1 g) of di-isopropylamine in 200 ml of dry ether was added 0.25 mol (16 g) n-butyl-lithium under a nitrogen atmosphere at 0 °C. To the reaction mixture was then dropwisely added 0.25 mol (29 g) of ethyl isobutyrate in 100 ml of dry ether. After stirring for 2 h, allowing warming to room temperature during the last hour, 0.125 mol (25.5 g) of 1,3-di-iodopropane was added dropwise. When the addition was completed the reaction mixture was refluxed for 12 h and then cooled. To the reaction mixture were added 150 ml water. The organic layer was separated and dried with $MgSO_4$ and then distilled, yield 18 g (53%), b.p. 56—58 °C at 0.3 mmHg (lit.,[12] 105—106 °C at 1.3 mmHg).



Scheme 2.

Diethyl 2,2,2′,2′-Tetramethyl-3,3′-oxydibutanoate.—To a mixture of 0.3 mol sodium hydride in 300 ml of dioxane was added 0.1 mol (18.2 g) of bromopivalic acid [14] and 0.1 mol (11.8 g) hydroxypivalic acid [14] in 200 ml of dioxane. A catalytic amount of sodium iodide was added and the reaction mixture was refluxed for *ca.* 100 h. The mixture was cooled on an ice-bath and acidified with 50% H_2SO_4. The reaction mixture was filtered and evaporated and the residue was recrystallized from acetic acid–light petroleum (b.p. 40—60 °C) (1 : 2). The yield of the diacid was 10%, m.p. 133—135 °C.

The diester was obtained by refluxing 0.06 mol (12 g) of the acid and 15 ml of ethanol in 100 ml of toluene in the presence of a catalytic amount of toluene-*p*-sulphonic acid. After the theoretical amount of water had separated (Dean–Stark trap), the reaction mixture was cooled and washed with a sodium hydrogen carbonate solution. Distillation gave the diester in 80% yield, b.p. 73—76 °C at 0.1 mmHg (lit.,[15] 73—75 °C at 0.1 mmHg).

N.m.r. Measurements.—The ^1H n.m.r. spectra were recorded on a JEOL model JNM-MH-100, or a Bruker model HX 270 spectrometer. The samples were *ca.* 0.5M solutions in CD_2Cl_2, $CHCl_2F$, or $(CD_3)_2CO$. Tetramethylsilane was added to provide the internal lock signal. The temperatures were measured as described elsewhere.[16]

Rate constants were evaluated by visual fitting of experimental to calculated spectra for at least five temperatures around the coalescence temperature. The free energies of activation were obtained from the Eyring equation.[17] For (III) a complete bandshape analysis was performed using the combined rate constants obtained from the temperature dependence of the geminal methyl signals and the ring methylene signals. The determination of the effective transverse relaxation time (T_2) was performed as previously described.[18]

Molecular Mechanics Calculations.—The calculations were performed using the MM2 computer program developed by Allinger and his co-workers.[19,20] This program does not include effects on bond lengths due to changes in π-conjugation. Such effects, however, seem to be small for the dicarbonyl unit. *Ab initio* calculations on glyoxal using complete structural optimizations and a large basis set (double zeta plus polarization) show small changes, less than or equal to 0.002 Å, of the central C–C and the C=O bond lengths upon rotation from the *s-trans* conformation to the calculated saddle point at a CO–CO dihedral angle of 74.7°.[21] This reflects very small changes in bond orders.

The parameters added to the MM2 program are given in Table 1.

Table 1. Force-field parameters [a]

Natural bond lengths and stretching force constants

Bond	l_0/Å	k_s/mdyn Å^{-1}
$C_{co}-C_{co}$ [b]	1.504	6.05

Natural bond angles and bending force constants

Angle	θ_0/°	k_θ/mdyn Å rad^{-2}
$C_{co}-C=O$	121.0	0.50
$C_{sp3}-C_{co}-C_{co}$	113.0	0.40
$H-C_{co}-C_{co}$	113.0	0.40

Torsional constants

Angle	V_2/kcal mol^{-1}	V_3/kcal mol^{-1}
$X-C_{co}-C_{co}-Y$ [c]	1.00	
$H-C_{sp3}-C_{co}-C_{co}$		−0.75
$C_{sp3}-C_{sp3}-C_{co}-C_{co}$		−0.33

Bond moment

Bond	μ/D
C=O	2.90

Fractional atomic charges

Atom	Charge	Ref.
C=*O*	−0.44	22
C=O	+0.34	22
C–C_{co}	+0.10	22
$C-\mathit{N}\langle^{C}_{C}$	−0.30	23
C–*O*–C	−0.28	23
C–*S*–C	−0.13	24
C–N	+0.10	23
C–O	+0.14	23
C–S	+0.06	24

[a] For notations see Ref. 19. [b] C_{co} = carbonyl carbon. [c] X, Y = O, H or C_{sp3}.

The geometry data used in the parametrization procedure were the electron diffraction geometries of *s-trans*-glyoxal[25,26] and biacetyl[4,5] and the microwave geometry of *s-cis*-glyoxal.[27] Unfortunately no electron diffraction geometry of *s-cis*-glyoxal or -biacetyl is available. Experimental and calculated geometries for *s-trans*- and *s-cis*-glyoxal and -biacetyl are given in Table 2.

The torsional V_2 term was evaluated by fitting the calculated rotational barrier for glyoxal to the experimental one.[6] The potential energy function thus obtained gives an energy difference between the *s-cis* and *s-trans* conformations of 3.5 kcal mol^{-1} in good agreement with experiments, 3.2 ± 0.6 (ref. 2) and 3.37 ± 0.43 kcal mol^{-1} (ref. 6) and a barrier to rotation of 5.0 kcal mol^{-1} at a dihedral angle of 75°.

Extending the calculations to biacetyl a rotational barrier of 4.1 kcal mol^{-1} at a dihedral angle of 0° (= *s-cis*) was calculated. In agreement with *ab initio* calculation[8] and the potential energy function obtained from dipole moment data,[29] the potential energy does not show any significant changes in the dihedral angle interval 0—40°. The calculated barrier to rotation for biacetyl is *ca.* 3.5 kcal mol^{-1} lower than was obtained from dipole moment data.[7,29] A lower barrier is to be expected since our calculated barrier corresponds to fully energy-minimized geometries, while the dipole moment data were interpreted using a rigid dicarbonyl geometry.

The molecular mechanics calculations described above all use the dipole–dipole approximation to calculate the electrostatic interactions. As this approximation is somewhat doubtful for dipoles at close distance, we have also used coulombic charge–charge interactions in the calculations. The atomic partial charges used were obtained from *ab initio* calculations and are given in Table 1. Using these charges the calculated rotational barrier for biacetyl becomes 6.9 kcal mol^{-1}. In all calculations an effective dielectric constant of 1.0 was employed.

Results and Discussion

Variable-temperature N.M.R. Spectra.—Ambient-temperature ^{1}H n.m.r. spectra of compounds (I)—(V) all display

Table 2. Calculated and experimental geometries for *s-trans*- and *s-cis*-glyoxal and -biacetyl

	Glyoxal				Biacetyl		
	s-trans		*s-cis*		*s-trans*		*s-cis*
Bond (Å) or angle (°)	Calc.	Exp.[25,26]	Calc.	Exp.[27,28]	Calc.	Exp.[5]	Calc.
$C_{co}-C_{co}$	1.518	1.525, 1.526	1.520	1.514	1.522	1.531	1.527
C=O	1.208	1.208, 1.212	1.209	1.207 (ass)	1.210	1.215	1.212
$C_{co}-H$	1.114	1.119, 1.132	1.114	1.130			
$C_{co}-CH_3$					1.515	1.517	1.518
$C_{co}-C=O$	121.9	121.6	124.5	123.4, 123.8	120.4	119.5	120.6
$C_{co}-C_{co}-H$	116.0	115.4	114.8	116.2, 115.5			
$C_{co}-C_{co}-CH_3$					116.5	116.6	120.4
H–C=O	122.1	123.0	120.7	120.4, 120.7			
$CH_3-C=O$					123.1	123.9	119.0
Dipole moment (D)			4.78	4.8[1]			

Table 3. ^{1}H N.m.r. data at slow exchange

Compound	Signal studied	Solvent	Temp. (K)	T_c/K	$\Delta\nu$/Hz	J_{AB}/Hz
(I)	CH_3	$CHCl_2F$	168	173	19.5 [a]	
(II)	CH_3	$CHCl_2F$	164	169	26.2	
(II)	CH_2	$CHCl_2F$	164	173	44.7	13.0
(III)	CH_3	$(CD_3)_2CO$	178	200	3.8	
(III)	CH_2	$(CD_3)_2CO$	178	217	21.5	14.8
(III)	CH_3	CD_2Cl_2	200	206	3.7	
(III)	CH_2	CD_2Cl_2	190	228	23.5	14.9
(IV)	CH_3	$CHCl_2F$	173	183	23.0	
(V)	CH_2	$CHCl_2F$	172	188	82.9	13.8

[a] 270 MHz spectrometer.

Table 4. Free energy barriers to inversion for compounds (I)—(V)

Compound	Signal studied	$\Delta G^{\ddagger}$ [a]/kcal mol^{-1}	Solvent	Temp. (K)
(I)	CH_3	8.7	$CHCl_2F$	168.0
(II)	CH_3	8.6	$CHCl_2F$	171.1
(II)	CH_2	8.6	$CHCl_2F$	171.1
(III)	CH_3	10.8 [b]	$(CD_3)_2C=O$	171.0
(III)	CH_2	10.8 [b]	$(CD_3)_2C=O$	211.9
(III)	CH_3	11.3	CD_2Cl_2	205.9
(III)	CH_2	11.3	CD_2Cl_2	228.7
(IV)	CH_3	9.1	$CHCl_2F$	181.4
(V)	CH_2	9.3	$CHCl_2F$	186.0

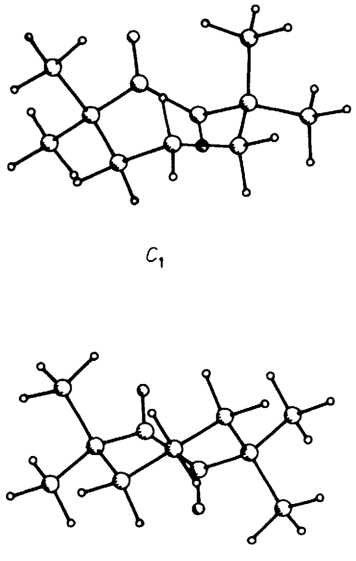
[a] Estimated error ± 0.1 kcal mol^{-1}. [b] $\Delta H^{\ddagger} = 10.8 \pm 0.1$ kcal mol^{-1}. $\Delta S^{\ddagger} = -0.1 \pm 0.3$ cal mol^{-1} K^{-1}. Only random errors calculated from the standard deviations in the Eyring plot are included.

a sharp singlet for the four methyl groups. At lower temperatures this signal broadens and finally, in the spectra of (I)—(IV), splits into a doublet. For compound (I) this splitting could only be observed in the 270 MHz spectrum, owing to a small shift and line broadening at the low temperatures required. For compound (V) no splitting of the methyl resonance signal was observed. This is probably due to a very small shift and also to interfering overlap by the $N-C(CH_3)_3$ signal. Compounds (II)—(V) have two isolated ring methylene groups that give rise to a sharp singlet at ambient temperature and in (II), (III), and (V) an AB pattern below coalescence. In the low-temperature spectrum of (IV) a small shift and strong overlap by the NCH_3 signal precluded the analysis of the methylene signals. No temperature dependence of the *N*-substituent signals was observed. Coalescence temperatures and chemical shifts and coupling constants at slow exchange are given in Table 3.

The AB shifts and also the methyl-group shifts vary considerably through the series of compounds. This variation may be attributed to the different magnetical anisotropies of the ring hetero substituents. The geminal coupling constants for the methylene groups in (II), (III), and (V) decrease, as expected, numerically with increasing electronegativity of the hetero-atom substituent.

Rate constants were evaluated from the temperature-dependent band shapes as described in the Experimental section. Free energies of activation were calculated using the Eyring equation. The energy data obtained are given in Table 4.

For compounds (II) and (III) it was possible to study the temperature dependence of two different sets of proton signals arising from the methyl and methylene groups, respectively. The free energies of activation obtained from the two sets of rate constants were identical within error limits, indicating that the temperature dependence of the n.m.r. spectrum corresponds to only one dynamic process.


C_1

C_2

Figure 1. Calculated lowest-energy conformations for compound (I)

Table 5. Calculated conformational energies [a] and carbonyl–carbonyl dihedral angles for compounds (I)—(V)

Compound	C_1 conformation (kcal mol^{-1})	CO–CO dihedral angle (°)	C_2 twist-boat (kcal mol^{-1})	CO–CO dihedral angle (°)
(I)	+0.80	94.5	0	95.4
(II)	0	87.2	+1.91	88.6
(III)	0	102.3	+1.08	102.1
(IV)	0	87.7	+1.63	90.9
(V)	0	87.5	+5.71	92.5

[a] Dipole approximation.

For (III) a total band-shape analysis was performed using the combined sets of rate constants. The activation entropy obtained does not significantly deviate from zero (cal mol^{-1} K^{-1}).

Conformations.—The compounds studied in this work may formally exist in a large number of conformations of the chair–twist-chair or boat–twist-boat families, in analogy with the different conformations in the pseudorotational scheme of cycloheptane as analysed by Hendrickson.[30] However, repulsive steric interactions between the two sets of geminal methyl groups and also electrostatic repulsion between the two carbonyl groups drastically reduce the number of low-energy conformers.

The n.m.r. data described above are only consistent with conformations having C_2 or C_s symmetries, possibly time-averaged, with the C_2 axis or the mirror plane bisecting the carbonyl groups. The C_s symmetry is less probable, since it requires eclipsing of the two carbonyl groups, maximizing the repulsive electrostatic interaction between the two oxygens. Furthermore, a carbonyl–carbonyl dihedral angle of 0° (*s-cis*) is inconsistent with u.v. data from which a dihedral angle of 90—110° has been inferred.[12]

Molecular mechanics calculations, performed as described in the computational section, indicate that only a small number of low-energy conformers are present. An extensive search of the potential energy surface using several different

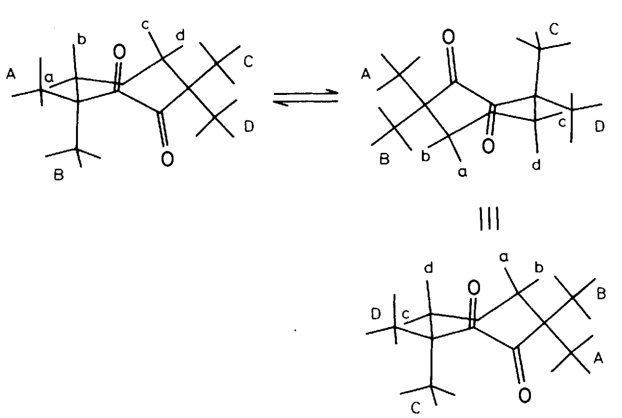


Figure 2. Scheme for pairwise exchange of the methyl groups and methylene protons in the C_1 conformation

trial input geometries resulted in the location of two low-energy local minima. The corresponding conformations are C_2 twist-boat and a slightly distorted chair conformation with C_1 symmetry. The computer-generated geometries of these conformations for (I) are shown in Figure 1. The corresponding conformational energies for compounds (I)—(V) are given in Table 5.

For (II)—(V) the C_1 conformer is calculated to be the preferred one. For (I) the C_2 twist-boat is of lowest energy with the C_1 conformation at 0.8 kcal mol^{-1} higher energy.

In both conformations of (I) the carbonyl–carbonyl dihedral angle is calculated to be close to 95° in agreement with conclusions from u.v. data [12] and 13° larger than predicted by Verheidt *et al.*[9]

Inspection of the calculated geometry of the twist-boat conformer of (I) shows that the bond lengths and bond angles for the C–CO–CO–C fragment are very close to the corresponding geometrical parameters calculated for biacetyl using the same dihedral angle. This means that compound (I), as far as the dicarbonyl unit is concerned, may serve as an accurate model for a *ca.* 95° twisted biacetyl molecule.

The calculated preference for the C_1 structure in compounds (II)—(V) is at first glance at variance with the n.m.r. data of these compounds at slow exchange (see Table 3). A C_1 symmetry should lead to four different methyl signals and two AB quartets in the n.m.r. spectra below the coalescence temperature.

However, pseudorotation provides a low-energy path for pairwise exchange of the methyl groups and methylene protons in the C_1 conformation, resulting in pairwise time-averaged methyl and methylene shifts in accordance with the number of signals observed in the low-temperature n.m.r. spectra. The scheme for the exchange is shown in Figure 2.

The free energy of activation for this pseudorotational process is too low to allow the process to be observed in the temperature-dependent n.m.r. spectra.

Barriers to Inversion.—The free activation energies to inversion of the seven-membered ring system in (I)—(V), given in Table 4, show only a small dependence of the barrier on the ring hetero substituent in (II), (IV), and (V). The introduction of a sulphur atom in (II), however, gives an increase in the barrier of *ca.* 2 kcal mol^{-1} when compared with the barrier of (I).

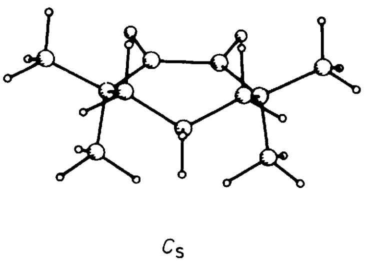


Figure 3.

Table 6. Molecular mechanics calculated inversion barriers [a] for compounds (I)—(V)

	Dipole–dipole model		Charge–charge model	
Compound	Calc. barrier	Electrostatic part	Calc. barrier	Electrostatic part
(I)	10.7	3.6	12.7	5.5
(II)	8.1	3.2	10.1	5.2
(III)	12.8	4.1	15.1	6.4
(IV)	9.2	3.3	11.2	5.3
(V)	9.4	3.2	11.5	5.3

[a] Energies in kcal mol^{-1}.

Using the molecular mechanics method a suitable transition-state structure for the inversion process was searched for, with the aid of the pseudorotational map of cycloheptane.[30] The inversion process in (I)—(V) requires a passage of the carbonyl groups and as this corresponds to a dicarbonyl arrangement with maximum repulsive electrostatic interaction between the two carbonyl oxygens, it was considered reasonable to assume an *s-cis* or close to *s-cis* conformation of the dicarbonyl unit in the transition state for the inversion process. The lowest-energy *s-cis* geometry found, a C_s chair conformation, is shown in Figure 3.

The corresponding C_s boat was calculated to be of 4.3—7.6 kcal mol^{-1} higher energy. Several pathways are, however, available for a (twist)-boat–(twist)-chair interconversion, which do not require an eclipsing of the carbonyl groups.

By calculating the conformational energy of the C_s chair conformer as a function of small stepwise changes of the CO–CO dihedral angle, this structure was shown to be a local energy maximum on the potential-energy surface.

The calculated inversion barriers are given in Table 6, which also shows the calculated electrostatic contributions to the total barrier, using two models for the calculation of the electrostatic interactions. The overall agreement between calculated and experimental barriers (Table 4) is quite satisfactory, the most significant differences being an over-estimation of the barriers in (I) and (III). The inversion barrier decreases with increasing polarity of the solvent as shown in Table 4 for compound (III). Such a solvent effect was also observed by Verheidt *et al.*[9] Considering the *s-cis*-conformation of the calculated transition state this effect is to be expected, the transition state of the inversion process being more polar than the initial state. The calculated barriers that refer to isolated molecules in the vapour phase should thus be higher than the experimental ones. The magnitude of the decrease of the barrier on going from vapour phase to a polar solvent should be proportional to the intercarbonyl dihedral angle in the initial state. As shown in Table 5, compounds (I) and (III) should thus be more sensitive to solvent polarity than the other compounds. For more accurate calculations on these strongly polar molecules a better description of the charge distribution, including all atoms, is probably required.

The calculated transition-state geometries for (I)—(V) indicate that the inversion process is accompanied by large changes in bond angles for the dicarbonyl unit. The C–CO–CO angle is increased by *ca.* 12°, while the two C–C–O angles are decreased by 4 and 8°, respectively. These angle bendings make up a significant part of the calculated steric contribution to the inversion barrier. The changes in bond angles are significantly different from those calculated for biacetyl. In this molecule the changes are +3.2, +0.5, and −3.7°, respectively, on going from a dihedral angle of 95 to 0° (*s-cis*). Thus, the ring system and the presence of geminal methyl groups on the ring forces the carbonyl oxygens to come closer to each other in the C_s chair transition-state structure of (I)—(V) than is the case in the *s-cis*-conformation of biacetyl. While the preferred conformation of (I) was found to be an accurate model for biacetyl with a dihedral angle of 95° the *s-cis*-chair conformation is appreciably different in geometry when compared with *s-cis*-biacetyl.

The electrostatic part of the barrier to inversion in (I)—(V) is calculated to be 42—52% of the total barrier. This is much larger than was found for the inversion of seven-membered cyclic oxamides, which were calculated to have initial and transition-state geometries in an overall similarity to those calculated for (I)—(V). The electrostatic contributions to the inversion barrier of the oxamides was calculated to be only 7—11%.[31] One reason for this difference is to be found in the different CO–CO dihedral angles in the lowest energy conformation. For the oxamides this was calculated to be only *ca.* 60°, resulting in a sizeable electrostatic repulsion already in the initial state of the inversion process of the seven-membered ring system.

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