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Conformational Analysis. Part 12.[1] A Theoretical and Lanthanide-induced Shift (LIS) Investigation of the Conformation of Benzophenone and 3,4′-Dichlorobenzophenone

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Conformational analysis of benzophenone and 3,4′-dichlorobenzophenone has been studied by theoretical (semiempirical and *ab initio*) calculations and by the lanthanide-induced shift (LIS) technique. The theoretical calculations were based on *ab initio* (STO-3G) energies of MNDO optimised geometries. The minimum-energy conformer is a helical conformer with a dihedral angle (θ) between the phenyl and carbonyl group planes of 36°. Analysis of the theoretical curves gave a two-fold potential barrier about this bond of 20.4 kJ mol^{-1} and further showed that the most likely rotation of the phenyl rings was *via* a disrotatory mechanism with a high-energy perpendicular intermediate ($\theta_1 = 0°$, $\theta_2 = 90°$) 5.4 kJ mol^{-1} above the ground state. The LIS investigation of benzophenone was inconclusive due to the molecular symmetry, all torsional angles giving good solutions. For the 3,4′-dichlorobenzophenone the more extensive data set allowed a precise analysis. The best agreement factor was found for 56% of the *trans* conformer with a torsional angle (θ) of 26°. The lanthanide was also unevenly populated about the carbonyl group, 55% being on the side of the *meta*-chloro ring, with values of r, φ, and ψ for the Ln–O geometry found to be 2.75 Å, 55—60° and 160—165°, respectively. These results can be explained on the basis of steric effects between the lanthanide and the phenyl rings together with different π densities in the two rings.

The conformation of benzophenone has been studied by a wide variety of experimental and theoretical methods, all of which have indicated the preferred conformation to be helical (rings twisted out of the central carbonyl plane in opposite directions) rather than gable (rings twisted in similar directions)[2] (Figure 1). A third conformational form has also been suggested,[3] having one ring planar to the carbonyl and the other ring twisted out of the plane by a large angle (about 70°). However, the experimental evidence is overwhelmingly in favour of the helical form with each ring twisted from the plane by the same angle, θ_1 and θ_2, respectively. The degree of twist is less certain, values ranging from 42° (from molar Kerr constants)[3] to 30° (by *X*-ray diffraction).[4] Similarly various theoretical treatments have failed to produce a constant value. An extended Hückel (EH) approach[5] gave a minimum-energy helical conformation having a twist angle of 38°, a CNDO/2 study by the same workers indicated the favoured conformation to be $\theta_1 = \theta_2 = 90°$. The tendency of NDO methods to fail for conjugated systems was more recently demonstrated by a study using MINDO/3, MNDO, and MNDOC, all of which indicated the low-energy conformer to be helical with twist angles of 89.7, 70.4, and 77.9°, respectively.[6] Very small energy differences were found between these conformers and the $\theta_1 = \theta_2 = 90°$ conformer, only 1.4 kJ mol^{-1} in the MNDO case and close to zero in the remainder. This is in contrast with an energy barrier of 14.1 kJ mol^{-1} for rotation *via* the 90° conformer found by the EH study. A recent evaluation of the energy barrier to rotation[7] using ^{13}C spin lattice relaxation times (T_1) produced a value of 11.5 kJ mol^{-1}. Rotation may not be occurring *via* the 90° conformer, however, indeed a modified C-INDO study[2] (which, in contrast to the above NDO methods, gave good agreement with experimental determinations of the twist angle—a value of 30° being indicated) suggested rotation would occur *via* the $\theta_1 = 0°, \theta_2 = 90°$ conformer.

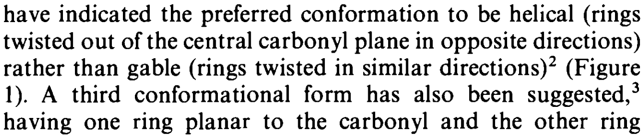


Figure 1. (a) Helical and (b) gable forms of benzophenone

Substituents in the 3 and 4 positions have generally been found to exert little influence on the preferred conformation, either in solution,[8,9] or in the solid phase, an *X*-ray study of 4,4′-dichlorobenzophenone[10] produced a twist angle of 29° (compared with 30° reported earlier for benzophenone). Generally, twist angles determined by similar methods have been of the same order for the parent molecule and substituted benzophenones. Grimaud *et al.*[9] carried out an extensive experimental study using a variety of techniques including optical anisotropy determinations, infra-red studies, and some lanthanide shift work [using Eu(dpm)$_3$ and proton spectra only]. The first of these methods[9a,9b] produced a twist angle of 31 ± 1° for benzophenone itself and a series of similar values for a number of chloro-substituted derivatives; 27° for the 4,4′-dichloro, 31.5° for the 4-chloro, and 31.5° for the 3-chloro. An interesting observation from the lanthanide study of 3,3′-dichlorobenzophenone[9c] was an apparent conformational preference for the *trans* conformer (with respect to the chlorine positions relative to the carbonyl) over the *cis* isomer (52—48%). The indicated twist angle in this case was 37°.

Our interest in the molecule results from the presence of a benzophenone-like unit in the commercially important poly(aryl ether ketone) polymers. In order to achieve reliable molecular modelling of the polymer chain it is necessary to know both the geometry and torsional potential around the phenylcarbonyl bonds. We present here both theoretical and experimental approaches to this problem, the theoretical *via* semiempirical (MNDO) and *ab initio* (STO-3G) calculations and the experimental *via* the lanthanide-induced shift technique.

Table 1. MNDO optimised geometry parameters and MNDO and STO-3G energies for helical[a] conformations of benzophenone

$\theta_1(=\theta_2)$[a] angle (°)	C=O bond length (Å)	C(1)–C(O) bond length (Å)	C(1)–C(O)–C(1′) angle (°)	MNDO[b] energy	STO-3G[c] energy
0.0	1.239	1.542	135.71	104.8	67.8
10.0	1.238	1.536	133.25	89.8	53.3
20.0	1.234	1.524	127.75	58.2	23.5
30.0	1.231	1.518	123.14	32.2	6.2
40.0	1.229	1.514	120.15	17.6	5.0
50.0	1.227	1.511	118.76	10.1	10.7
60.0	1.226	1.510	118.04	6.6	17.7
70.0	1.225	1.510	117.61	5.3	23.8
80.0	1.224	1.510	117.46	5.0	28.2
90.0	1.224	1.510	117.41	5.0	29.9
30.0[d]	1.237	1.532	132.48	76.0	54.7
60.0[d]	1.229	1.518	123.08	24.9	32.5

[a] Unless indicated otherwise. [b] Quoted energy = (M × 96.485) + 5.0 kJ mol^{-1}, where M is the energy difference (in eV) between a conformer and the 80.0° form. [c] Quoted energy = (G × 2 625.01) + 5.0 kJ mol^{-1}, where G is the energy difference (in a.u.) between a conformer and the 40.0° form. [d] Gable conformation: (1) θ_1 = 30°, θ_2 = 150°, (2) θ_1 = 60°, θ_2 = 120°.

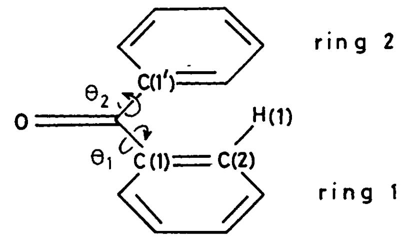


Figure 2. Illustration of method of ring rotation used in the theoretical study

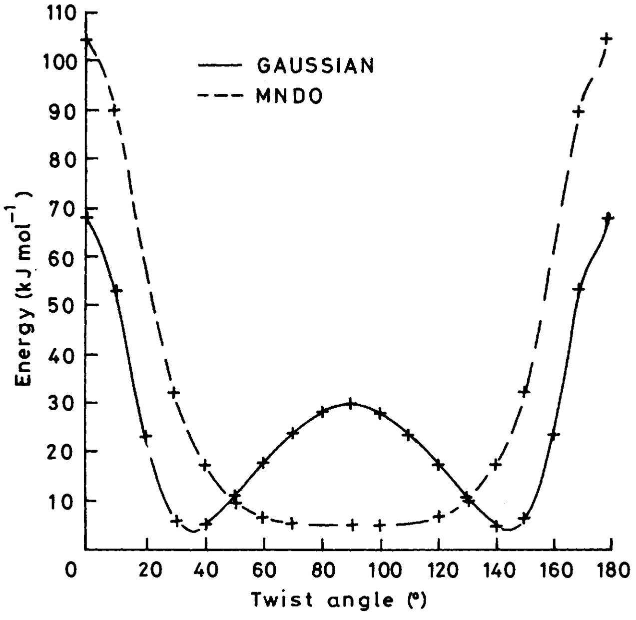


Figure 3. Energy *vs.* conformation for benzophenone

Conformational analysis of molecules in solution by means of lanthanide-induced shifts is a well established technique which has been applied to a wide variety of substrates.[11,12] The method involves the experimental determination of pseudo-contact shift values ($\delta\Delta$) for both C and H atoms, these values generally being quoted for a lanthanide shift reagent (L): substrate (S) molar ratio of 1:1 (ρ = [L]/[S] = 1). Experimentally values of $\rho \leqslant 0.2$ are used, since in this region the ρ *vs.* observed shift relationship is a linear one and $\delta\Delta$ can be obtained from the slope of this plot. The LIS (ΔM) is not purely a pseudo-contact shift but contains contributions from two other sources, namely a contact shift [considered negligible for Yb(fod)$_3$] and a diamagnetic shift (ΔD) [estimated from shifts obtained with complexation of La(fod)$_3$ for C atoms, but considered negligible for H atoms].

The $\Delta M - \Delta D$ values obtained from the above method are then compared with those calculated from the McConnell–Robertson equation[13] where r_i is the distance between the

$$\delta\Delta = x(3\cos^2\theta - 1)/r_i^3 \qquad (1)$$

lanthanide and atom i, x is a constant for the system, and θ is the O–Ln–atom i angle for various conformations of the substrate–lanthanide complex. The method can provide information on the molecular conformation and conformational isomerism in solution.

Theoretical

(i) *Preferred Conformation of Benzophenone.*—Analyses using the MNDO method[14,15] and GAUSSIAN76 (STO-3G basis set)[16,17] were carried out, the results of which are presented in Table 1. Ring rotations are measured as angles of twist from the planar form where θ_1 is the degree of twist of ring 1 in a clockwise direction [as viewed from C(1) to C(O)] and θ_2 is the degree of twist of ring 2 in an anticlockwise direction [viewed from C(O) to C(1′)], see Figure 2.

An initial MNDO optimisation of the C=O and C(1)–C(O) bond lengths and the C(1)–C(O)–C(1′) bond angle produced a geometry which was then used in the GAUSSIAN76 programme. Little change is seen in these parameters for all conformations other than in those approaching planarity (see Table 1). As expected, MNDO predicts a preferred conformer with twist angle close to 90°. The result, similar to that observed in a previous study,[6] is an example of the failure of MNDO to correctly account for conjugation energy. STO-3G, in contrast, predicted a well defined minimum-energy conformation with a twist angle of 36° (see Figure 3), corresponding to an energy of 4.3 kJ mol^{-1} on the STO-3G scale used in Table 1. The MNDO optimised parameters for this conformer were 1.230 Å (C=O), 1.515 Å [C(O)–C(1)], and 121.28° C(1)–C(O)–C(1′).

Similar calculations were performed for the 30° and 60° gable conformers (θ_1 = 30°, θ_2 = 150° and θ_1 = 60°, θ_2 = 120°, respectively). Both MNDO and STO-3G predict these forms to be considerably higher in energy than the equivalent helical forms, the expected result (Table 1).

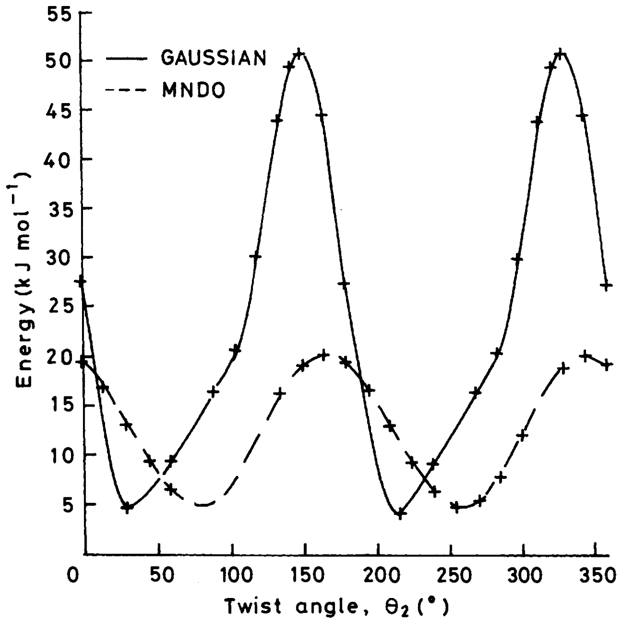


Figure 4. Energy barrier to ring rotation by a conrotatory mechanism using MNDO ($\theta_1 = 80°$) and GAUSSIAN76 ($\theta_1 = 36°$)

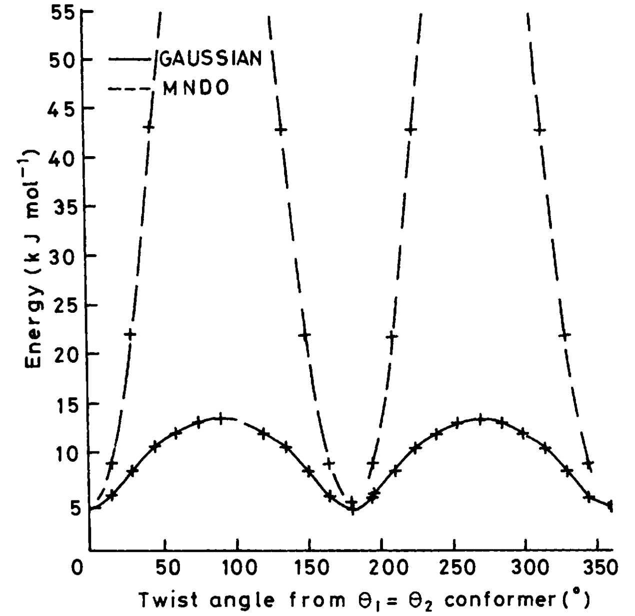


Figure 5. Energy barrier to ring rotation by a disrotatory mechanism using MNDO [$(90 - \theta_1) + (90 - \theta_2) = 20°$] and GAUSSIAN76 [$(90 - \theta_1) + (90 - \theta_2) = 108°$]

The above calculations were carried out assuming no change would occur in the geometry of the rings on rotation. In practice this is found to be incorrect, as the following calculation on the planar conformer indicates. MNDO optimisation of the C(O)–C(1)–C(2) and C(1)–C(2)–H(1) angles (in addition to those parameters previously optimised) produced values of 124.72° and 123.33°, respectively. A value of 130.42° was indicated for the C(1)–C(O)–C(1′) angle, considerably smaller than that given by the more rigid optimisation (135.71°). The STO-3G energy of this geometry was calculated to be 44.6 kJ mol^{-1}, some 23.2 kJ mol^{-1} lower than that found for the more rigid planar conformer. However, this conformation is by far the highest in energy and thus similar calculations performed on other conformers might be expected to produce less significant differences, indeed for conformations where steric effects are small no significant energy difference between the two methods is likely to be observed. Since it is these latter conformations which are of importance in the following consideration of energy barriers (the planar conformer is a very unlikely intermediate) and rotational potentials the more rigid optimisations are considered to give an adequate assessment of the total energy.

(ii) *Energy Barrier to Ring Rotation*.—There are two possible mechanisms by which ring rotation in benzophenone may occur, involving either conrotatory or disrotatory movement of the rings. Figure 3 is an example of one conrotatory model; both MNDO and STO-3G indicate that the rotation will occur *via* the $\theta_1 = \theta_2 = 90°$ conformer, rather than through the planar conformer. However, whilst STO-3G suggests a barrier of some 25 kJ mol^{-1} (6 kcal mol^{-1}), MNDO predicts the same barrier to be close to zero.

The conrotatory mechanism was further studied by using the preferred conformers from the previous section. With θ_1 fixed at 80° and 36° for the MNDO and STO-3G studies, respectively, a similar MNDO optimisation to that used in the previous section [optimisation of C=O and C(1)–C(O) bond lengths and the C(1)–C(O)–C(1′) angle] was carried out for a series of θ_2 angles from 0—180°. STO-3G energies were then calculated for the optimised geometries of the $\theta_1 = 36°$ conformers. The results of this analysis are presented in Figure 4.

Barriers to rotation, as shown in Figure 4, are predicted to be 15.5 kJ mol^{-1} (3.7 kcal mol^{-1}) by MNDO and 47 kJ mol^{-1} (11.2 kcal mol^{-1}) by STO-3G. The poor agreement in the height of the energy barrier is further compounded by the difference in the conformations predicted to be the high-energy forms. MNDO suggests the $\theta_1 = 80°$, $\theta_2 = 170°$ (equivalent to a gable conformation of twist angles 80 and 10°) is of highest energy whereas STO-3G indicates the $\theta_1 = 36°$, $\theta_2 = 150°$ (gable conformation, angles of 36 and 30°) conformer is the higher-energy form. The gable conformer with $\theta_2 = 180 - \theta_1$ might have been expected to be of highest energy; however, this is found to be less energetic than the above conformations by 13.1 kJ mol^{-1} (MNDO) and by 1.4 kJ mol^{-1} (STO-3G). The latter result seems more reasonable and it is interesting that the $\theta_2 = 180 - \theta_1$ form is close to, but not at, the high-energy point. A similar conclusion was reached for the conrotatory mechanism proceeding by the $\theta_1 = \theta_2 = 90°$ conformer.[1]

The disrotatory mechanism could involve the perpendicular conformation ($\theta_1 = 0°$, $\theta_2 = 90°$) as the intermediate. MNDO predicts a barrier of 13.6 kJ mol^{-1} and STO-3G one of 5.4 kJ mol^{-1} for this model.

A further possibility is for rotation to occur so as to maintain a similar angle between the rings to that found in the preferred conformer (20° by MNDO, 108° by STO-3G). The results of this analysis, carried out in a similar manner to those previously described, are shown in Table 2 and Figure 5. Once again only small variations were seen in the MNDO optimised bond lengths of conformers in the STO-3G study; however in the MNDO study some lengthening did occur from initial values of 1.224 Å (C=O) and 1.510 Å [C(1)–C(O)] in the 80° helical conformer to 1.237 Å and 1.537 Å in the conformer with each ring twisted 90° from the initial position. Since this latter conformation is close to planarity this behaviour is entirely consistent with that seen in section (i).

Both MNDO and STO-3G predict that the high-energy conformer of the disrotatory model will be one in which the rings are twisted 90° from their positions in the 80° (MNDO) and 36° (STO-3G) helical conformers. In the MNDO case this is very much the expected result since this is also the conformer which is closest to planarity, it is equivalent to a helical conformation of $\theta_1 = \theta_2 = 10°$. Given the already mentioned failing of MNDO to account for conjugation it is not surprising that the energy barrier predicted, 84.8 kJ mol^{-1}, is excessively

Table 2. Energy barriers to ring rotation by a disrotatory mechanism, MNDO and STO-3G studies. MNDO optimised C=O[a] and C(1)–C(O)[b] bond lengths and C(1)–C(O)–C(1′) angle for each conformation

MNDO				STO-3G			
θ_1	θ_2	C(1)–C(O)–C(1′)	Energy[c]	θ_1	θ_2	C(1)–C(O)–C(1′)	Energy[d]
80.0	80.0	117.46	5.0	36.0	36.0	121.28	4.3
95.0	65.0	118.44	9.0	51.0	21.0	121.18	5.6
110.0	50.0	121.68	22.2	66.0	6.0	121.04	8.2
125.0	35.0	126.40	43.0	81.0	−9.0	120.54	10.6
140.0	20.0	130.28	65.6	96.0	−24.0	119.62	12.0
155.0	5.0	132.48	83.1	111.0	−39.0	118.92	13.1
170.0	−10.0	133.22	89.8	126.0	−54.0	118.58	13.5

[a] 1.230 ± 0.007 Å (MNDO), 1.228 ± 0.003 Å (STO-3G). [b] 1.524 ± 0.014 Å (MNDO), 1.514 ± 0.003 Å (STO-3G). [c] Based on similar scale to that used for MNDO energies in Table 1. [d] Based on similar scale to that used for STO-3G energies in Table 1.

Table 3. Comparison of energies calculated using MNDO/STO-3G (E_C) and from rotational potentials (E_V)

θ_1	θ_2	E_C[a]	E_V[a]	$E_C - E_V$
0.0	0.0	67.8	−10.8	78.6
36.0	36.0	4.3	3.3	1.0
60.0	60.0	17.7	19.8	−2.1
90.0	90.0	29.9	30.0	−0.1
0.0	36.0	27.6	−3.8	31.4
0.0	90.0	9.7	9.6	0.1
36.0	90.0	16.5	16.6	0.1

[a] Based on similar scale to that used for STO-3G energies in Table 1.

large. The STO-3G study produces a more interesting result, indicating a barrier of 9.2 kJ mol^{-1} (2.2 kcal mol^{-1}), the high-energy conformer being equivalent to a helical conformer of $\theta_1 = \theta_2 = 54°$. Intermediate helical conformations where θ_1 does not equal θ_2 are predicted to be lower in energy. The perpendicular conformer previously mentioned is 3.8 kJ mol^{-1} less energetic than the above high-energy form.

(iii) *Rotational Potentials.*—Internal rotation in molecules can be separated into one-fold (V_1), two-fold (V_2), and three-fold (V_3) components,[18] the relative importance of each depending on the molecular structure. In benzophenone rotation of one ring around the C(1)–C(O) bond may be described by a simple two-fold potential, given by equation (2),

$$E(\theta) = V_0 = V_2(1 - \cos 2\theta)/2 \qquad (2)$$

where E is the energy of a particular conformation, θ is the angle of twist from the carbonyl plane, and V_0 is a constant depending on the energy scale chosen.

In order to evaluate V_2 and V_0 a series of MNDO and STO-3G calculations were performed varying θ_2 with $\theta_1 = 90°$, using a similar procedure to that previously described. This particular series of conformers was chosen to minimise the steric contribution to the overall energy, the MNDO optimised geometries showing the extent to which this was achieved. For example, the C(1)–C(O) bond length was only 0.004 Å longer in the $\theta_2 = 90°$ conformer (which might be expected to be the most sterically hindered) than in the $\theta_2 = 0°$ conformer (1.511 and 1.515 Å, respectively). The C(1)–C(O)–C(1′) angle was $\leqslant 120.0°$ for all conformations considered.

From the above, a value of 20.4 kJ mol^{-1} for V_2 was obtained. In order to account for the simultaneous rotation of both rings, however, it is necessary to modify equation (2) as follows:

$$E(\theta_1, \theta_2) = V_0 + V_2(1 - \cos 2\theta_1)/2 + V_2(1 - \cos 2\theta_2)/2 \qquad (3)$$

where θ_1 and θ_2 are the respective twist angles previously defined (Figure 2). In this format the value of V_0 is −10.8 kJ mol^{-1} for the energy scale chosen.

Equation (3) can now be used to calculate conformational energies, and these values may be compared with those obtained from MNDO/STO-3G calculations. The results (Table 3) indicate that equation (3) adequately reproduces calculated energies for conformers in which there is no significant steric contribution to the overall energy. The planar form is predicted to be the low-energy conformer, the correct result when only conjugational factors are considered. The $E_C - E_V$ term gives a crude approximation of the steric energy.

Experimental

Commercial samples of benzophenone (Aldrich) and 3,4′-dichlorobenzophenone (I.C.I.) were recrystallised from light petroleum (b.p. 60—80 °C) prior to use. The LIS experiments were carried out using the incremental weighing method in which weighed amounts of shift reagent are added to a known mass of substrate. ^{1}H and ^{13}C n.m.r. spectra were recorded at 250 MHz and 62.8 MHz respectively on a Bruker WM 250 spectrometer at ambient temperature. The solvent used, $CDCl_3$, was dried over molecular sieves and the shift reagents, substrates, and all apparatus used were dried *in vacuo* over P_4O_{10} for 24 h prior to use.

Correlation coefficients obtained from ρ *vs.* observed shift plots for each atom were of the order 0.9980—0.9990 for benzophenone and 0.9960—0.9970 for 3,4′-dichlorobenzophenone, suggesting some deviation from linearity over the range considered ($\rho < 0.2$). The calculated intercept values, δ_{INT}, (from the best straight line fit) shown in Tables 4 and 5 are all larger than the observed shifts of the spectra recorded at $\rho = 0$ (*i.e.* no lanthanide shift reagent added). Furthermore, removal of the $\rho = 0$ point produces an improvement in the correlation coefficients (average values >0.9990 for benzophenone and >0.9980 for 3,4′-dichlorobenzophenone). Both these observations indicate non-linearity at very low shift reagent concentrations ($\rho < 0.02$).

Exclusion of the $\rho = 0$ point does not, however, significantly effect the relative ΔM values and as it is these, rather than the absolute values, which are used in the LIRAS3 analysis, inclusion of this point was considered to be justified.

(i) *Results.*—Observed chemical shifts (δ), diamagnetic shifts (ΔD), LISs (ΔM), and pseudo-contact shifts ($\Delta M - \Delta D = \delta\Delta$) for benzophenone (**1**) are shown in Table 4 with the equivalent information for 3,4′-dichlorobenzophenone (**2**) given in Table 5.

Comparison of observed $\delta\Delta$ values with values calculated for various lanthanide positions and substrate conformations was carried out using the LIRAS3 programme.[19] Calculation of an agreement factor, R, for each position and conformation allows

Table 4. Observed ^{13}C and ^{1}H shifts (δ), diamagnetic shifts (ΔD), intercept values (δ_{INT}), LISs (ΔM), and pseudo-contact shifts ($\Delta M - \Delta D$) for benzophenone (in p.p.m.)

	C-1	C-2	C-3	C-4	C=O
$\delta^{a,b}$	137.63	129.96	128.22	132.31	196.56
ΔD^{c}	−2.47	2.42	−0.04	2.07	6.71
δ_{INT}	137.90	130.11	128.27	132.35	197.19
ΔM^{d}	56.28	32.78	12.42	11.06	129.49
$\Delta M - \Delta D$	58.75	30.36	12.46	8.99	122.78

	1-H	2-H	3-H
δ^{b}	7.79	7.46	7.57
δ_{INT}	7.95	7.49	7.60
ΔM^{d}	31.25	6.10	5.10

[a] Shifts referenced to $CDCl_3$ (77.0 p.p.m.). [b] Shifts from TMS. [c] Three additions of La(fod)$_3$, ρ = 0.0437, 0.1284, 0.1567. [d] Four additions of Yb(fod)$_3$, ρ = 0.0183, 0.1001, 0.1240, 0.1864.

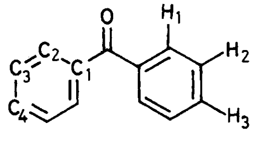
Table 5. Observed ^{13}C and ^{1}H shifts (δ), diamagnetic shifts (ΔD), intercept values (δ_{INT}), LISs (ΔM), and pseudo-contact shifts ($\Delta M - \Delta D$) for 3,4′-dichlorobenzophenone (in p.p.m.)

	C-1	C-2	C-3	C-4	C-5	C-6
$\delta^{a,b}$	138.87	129.72	134.70	132.52	129.72	127.89
ΔD^{c}	−1.34	1.14	−0.01	1.34	0.12	1.45
δ_{INT}	139.16	129.88	134.76	132.57	129.77	128.05
ΔM^{d}	53.06	29.42	11.62	9.72	11.09	30.60
$\Delta M - \Delta D$	54.40	28.28	11.63	8.38	10.97	29.15

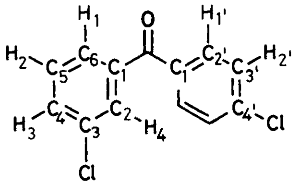
	C-1′	C-2′	C-3′	C-4′	C=O
$\delta^{a,b}$	135.21	131.35	128.79	139.34	193.90
ΔD^{c}	−1.22	1.47	0.08	1.88	4.46
δ_{INT}	135.50	131.52	128.85	139.40	194.54
ΔM^{d}	54.13	31.19	11.92	11.07	123.15
$\Delta M - \Delta D$	55.35	29.72	11.84	9.19	118.69

	1-H	2-H	3-H	4-H	1′-H	2′-H
δ^{b}	7.64	7.43	7.56	7.75	7.75	7.48
δ_{INT}	7.79	7.46	7.58	7.90	7.90	7.51
ΔM^{d}	29.18	5.00	4.53	26.88	29.87	5.62

[a] Shifts referenced to $CDCl_3$ (77.0 p.p.m.). [b] Shifts from TMS. [c] Four additions of La(fod)$_3$, ρ = 0.0355, 0.0748, 0.1335, 0.1864. [d] Four additions of Yb(fod)$_3$, ρ = 0.0421, 0.0542, 0.1036, 0.1393.



(1)



(2)

an assessment of the molecular conformation in solution to be obtained.

A four-site lanthanide complexation model was used in the analysis, allowing the lanthanide site to be reflected in the xy and xz planes (Figure 6). Variation of the percentage of lanthanide complexed on either side of the carbonyl group, *i.e.* across the xz plane, can be carried out. However, the benzophenone molecule is symmetrical about this plane and thus equal populations were assumed. Unsymmetrical substitution of the rings destroys the plane of symmetry and requires the possibility of an uneven population distribution to be considered.

Analysis of the above data was carried out using the geometry parameters shown in Table 6. These were assumed to be unchanged for the chlorinated compound.[8] Individual benzene ring planarity and C(1)–C(O)–C(1′) planarity were further assumed.

(a) *Benzophenone.* Starting from the planar form, the rings were rotated in a conrotatory manner in 10° increments until the 90° conformer was reached. It became apparent that the number of $\delta\Delta$ values available (five ^{13}C and three ^{1}H atoms) was insufficient to produce a well determined solution, indeed all conformations produced reasonable agreement (agreement factor $R < 2.0\%$) for lanthanide binding sites having Ln–O 2.75—2.85 Å, φ 70—90°, ψ 150—160° and (as explained earlier) equal occupation of all sites. The problem arises because the

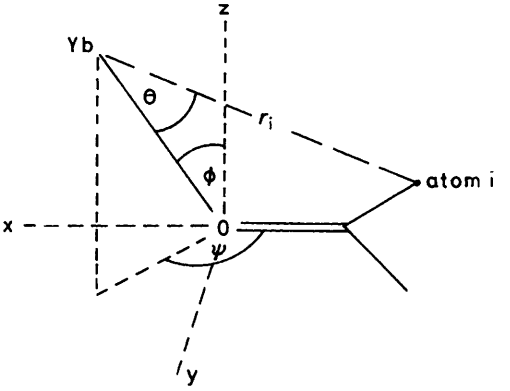


Figure 6. Illustration of parameters used in equation (1) and the LIRAS3 analysis

Table 6. Geometry parameters used in the LIRAS3 analysis

Parameter		Value
Bond lengths (Å);	C=O	1.210[a]
	C(1)–C(O)	1.481[a]
	C–C in ring	1.400
	C–H	1.080
	C–Cl	1.726[a]
Bond angles (°);	C–C(O)–C	120.9[a]
	C(2)–C(1)–C(O)	120.0
	C–C–C in ring	120.0
	H–C–C	120.0

[a] Values taken from reference 10.

Table 7. Comparison of equivalent δ*M* values of benzophenone and 3,4′-dichlorobenzophenone expressed as a percentage of their respective $\delta M_{C=O}$ values

Atom type	Benzophenone		3,4′-dichlorobenzophenone[a]	
	δ*M*	% of $\delta M_{C=O}$	δ*M*	% or $\delta M_{C=O}$
C=O	129.5	100.0	123.2	100.0
C-1	56.3	43.5	53.6	43.5
C-2	32.8	25.3	30.6	24.8
C-3	12.4	9.6	11.6	9.4
C-4	11.1	8.6	10.4	8.4
1-H	31.1	24.2	28.9	23.5

[a] Averaged values. Comparison of 2-H and 3-H is not possible due to the substituents in these positions in 3,4′-dichlorobenzophenone.

positions of four of the nuclei (C-1, C-4, 3-H, and $C_{C=O}$) are unaffected by ring rotation whilst the remaining four, whose positions do change, each have an overall LIS which is an average of the individual shifts of the equivalent nuclei on opposite sides of the ring. Thus the calculated LIS values for different conformations are unchanged for four atoms and only slightly changed for the other four atoms, making an assessment of the preferred twist angle impossible from the above analysis.

(b) 3,4′-*Dichlorobenzophenone*. In view of the above it was decided to use a substituted benzophenone in order to obtain a value for the twist angle in the parent molecule, assuming the substituent(s) do not significantly change the preferred conformation. For this assumption to be valid and to overcome the problems encountered above the chosen molecule had to meet certain criteria when compared to benzophenone itself; (a) a similar steric interaction between the rings, this clearly excludes *ortho* substitution; (b) a similar conjugative interaction between the rings, maintenance of similar π electron density in each ring; (c) production of non-equivalence between previously equivalent atoms, both within each ring and in opposite rings, thus an unsymmetrical substitution is favoured and (d) substituent(s) must not contain a potential lanthanide-binding site.

3,4′-Dichlorobenzophenone meets all the above requirements. A comparison of the δ*M* values for benzophenone and 3,4′-dichlorobenzophenone (Tables 4 and 5) clearly indicates a difference between the respective values for equivalent atoms. However, when each set are expressed as a percentage of their C=O δ*M* values then good agreement is obtained (Table 7). This observation indicates that the chloro substituents have no significant effect on the preferred molecular conformation and do not influence the lanthanide–substrate geometry to any great extent (the population distribution of the lanthanide between favoured sites is affected, see later). It therefore seems reasonable to assume that the preferred twist angle obtained for 3,4′-dichlorobenzophenone will be similar to that found in benzophenone itself.

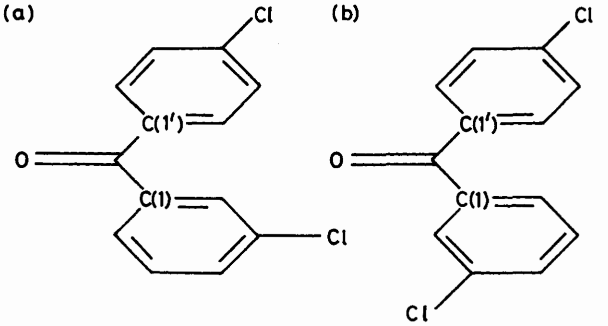


Figure 7. Planar forms of 3,4′-dichlorobenzophenone, (a) *trans* and (b) *cis* conformations

LIRAS3 analysis was carried out in a similar way to that described for benzophenone. However, a complication arises in that there are now two possible conformations (*cis* and *trans* with respect to the *meta* Cl/C=O positions) for a given twist angle. Using the planar *trans* form as the starting point [Figure 7(a)] the twist angle was varied from 0—180° (the planar *cis* form, Figure 7(b)] for a variety of conformer ratios. A 60:40 conformer ratio, for example, refers to a 60% *trans*, 40% *cis* distribution for twist angles 0—90° and a 60% *cis*, 40% *trans* distribution for twist angles 90—180°.

The series of analyses described above produced, for each conformer ratio, a minimum agreement factor, *R*, at a particular twist angle and lanthanide position. The best *R* values were found for conformer ratios in the 60:40—50:50 region, at twist angles 20—30°. In all these cases the position of the lanthanide was approximately the same, values of φ = 55—60° and ψ = 160—165° with a Ln–O distance of 2.75 Å. An uneven distribution of lanthanide was indicated, 55% being bound on the *meta*-chloro side of the carbonyl and 45% on the *para*-chloro side. This observation will be considered further below.

Figure 8 shows a series of plots of agreement factor *vs.* twist angle for various conformer ratios using the above lanthanide geometry (with averaged values of φ = 57° and ψ = 162°). In each case two minima are seen, the lower one occurring when the *trans* conformer predominates (twist angle = $\theta_{OPT} < 90°$) and the second for an angle $(180 - \theta_{OPT})°$ (for the 50:50 case the θ and 180 − θ conformations are equivalent). The value of θ_{OPT} decreases from 50° for a 100:0 conformer ratio (not shown in Figure 8) to about 25° for the 50:50 situation. A plot of the minima at different conformer ratios indicates that 3,4′-dichlorobenzophenone in chloroform exists 56% in the *trans* form (see Figure 9). The twist angle at this conformer ratio is 26°.

(ii) *Discussion*.—The indicated lanthanide position can be rationalised in the following manner. For the *trans* conformation two of the four lanthanide sites are favourable (sites 1 and 4, Figure 10) and two are unfavourable (2 and 3) if minimisation of steric interactions with the rings is considered to be the major factor in the positioning of the lanthanide, a conclusion that has been reached in many previous studies.[20,21]

For the *cis* conformation sites 2 and 3 will be favourable whilst sites 1 and 4 become unfavourable, thus, on average, all four sites will be occupied with 28% of bound lanthanide in each of sites 1 and 4 and 22% in each of 2 and 3 (the percentage occupation reflecting the presence of 56% of the *trans* form). This, however, assumes there is no preference for site 1 over site 4 (or *vice versa*) and equally for site 2 over site 3 (or *vice versa*). If this assumption holds then 50% of the lanthanide should be bound on each side of the carbonyl, but the LIRAS3 analysis indicated preferential binding on the side of the *meta*-substituted ring (55%).

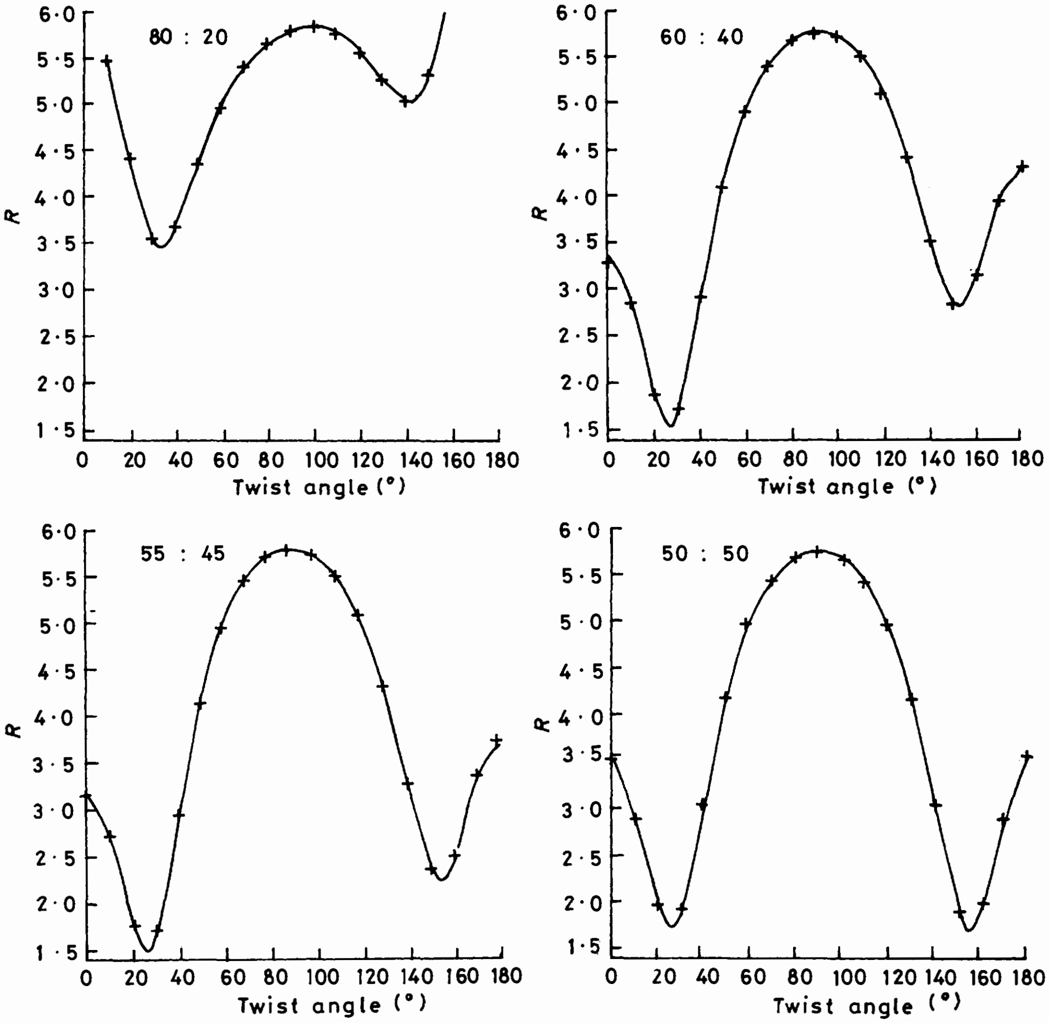


Figure 8. Plots of agreement factor, *R*, *vs.* twist angle for various conformer ratios of 3,4′-dichlorobenzophenone. (Ln–O = 2.75 Å, φ = 57°, ψ = 162°; 55% Ln on *meta* side of the carbonyl)

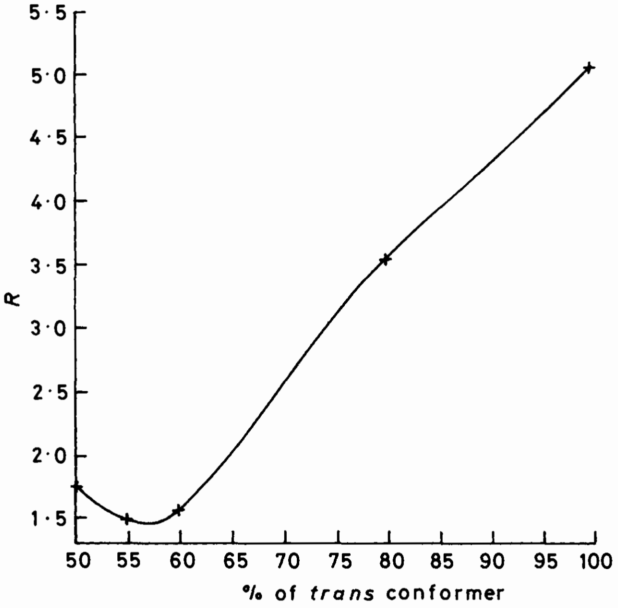


Figure 9. Plot of minimum agreement factors at various conformer ratios of 3,4′-dichlorobenzophenone. (Ln–O = 2.75 Å, φ = 57°, ψ = 162°; 55% Ln on *meta* side of the carbonyl)

A comparison of 'equivalent' nuclei on the two rings also suggests that there must be an uneven lanthanide distribution on each side of the carbonyl group. Averaging of the $\delta\Delta$ values in the *meta*-chloro ring is necessary for a reasonable comparison and when this is performed the $\delta\Delta$ values of the carbon atoms in this ring are all about 2—3% smaller than the values for the corresponding carbons in the *para*-substituted ring. This effect is reproduced computationally for a 55:45 (*meta*:*para*) population ratio of the lanthanide. This result indicates the importance of the $3\cos^2\theta$ term in the McConnell–Robertson equation, from a simple consideration of the distance (r_i) term the relative $\delta\Delta$ values indicate an excess of lanthanide on the *para*-chloro ring side of the carbonyl.

The uneven distribution of the lanthanide across the carbonyl group is most reasonably attributed to slight differences in the π electron density in the respective rings. A further consideration may be a degree of electrostatic attraction to the *meta*-chloro atom when the substrate is bound in the *cis* conformation. However, the lanthanide to chlorine distance is large so this is perhaps unlikely.

The combination of steric effects combined with conformational preferences (*i.e. trans vs. cis*) in solution and π density differences in the two rings results in unequal occupation of all four sites, the percentage of lanthanide in each being 25% (site 1), 24% (site 2), 20% (site 3), and 31% (site 4), see Figure 10. Thus site 4 is the most favoured binding site since it is sterically

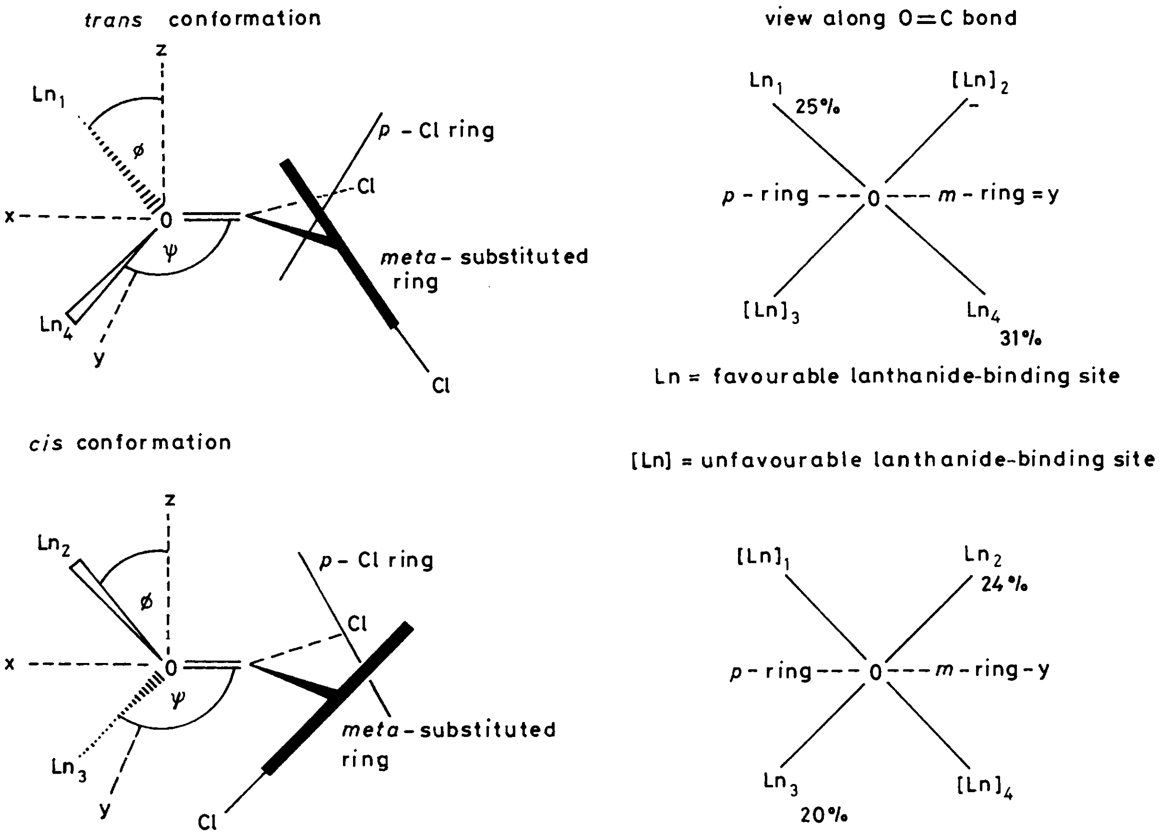


Figure 10. Lanthanide-binding sites in 3,4′-dichlorobenzophenone

favoured in the *trans* conformer and is also situated on the *meta*-chloro ring side of the carbonyl. Conversely site 3 is sterically favoured when the molecule is in the less abundant *cis* conformation and is situated on the *para*-chloro ring side of the carbonyl. Hence site 3 is the least occupied binding site. Application of the same arguments to sites 1 and 2 shows them to meet one of the two conditions for a favoured site and one of the two conditions for an unfavoured site, this being reflected in their percentage occupation being intermediate between those of site 3 and site 4.

Conclusions

Comparison of the relative δM values for benzophenone and 3,4′-dichlorobenzophenone shown in Table 7 indicates that the *meta* and *para* substituents exert no significant effect on the preferred conformation. The difference in the absolute values is most likely to be due to small variations in the experimental conditions rather than any change of lanthanide-binding site brought about by conformational changes in the substituted compound.

The theoretical value of θ predicted using an STO-3G basis set in GAUSSIAN76 (36°) is in reasonable agreement with the experimentally derived value (26°) and both methods produce figures similar to those obtained in previous studies. The *trans* conformer of 3,4′-dichlorobenzophenone was found to be the predominant form in solution (56%:44%), however, attempts to relate this to the respective energies of the *cis* and *trans* conformers were unsuccessful, MNDO calculating them to be of the same energy and the presence of the chloro substituents making the molecule too large to be used in GAUSSIAN76.

The theoretical calculations indicated that MNDO alone cannot correctly predict conformational preferences in conjugated systems. The combination of MNDO optimised geometries and STO-3G energies seems to be a reasonable approach to this problem. A comparison of Figures 4 and 5 suggests that ring rotation will occur *via* a disrotatory mechanism (MNDO predicts the conrotatory mechanism to be more likely) and the calculated energy of the $\theta_1 = 0°$, $\theta_2 = 90°$ conformer (9.7 kJ mol^{-1}) indicates that it might be the high-energy intermediate of the pathway.

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