Conformational Behaviour of Organic Carbonyl Compounds. Part 2.[1] Aldehydes and Acetyl Derivatives of Condensed Aromatic Hydrocarbons

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The relative conformer stability in a number of acetyl and formyl derivatives of condensed hydrocarbons has been determined by the lanthanide induced shift (LIS) method and by simulating the experimental chemical shifts. For the aldehydes of naphthalene the conformational results were confirmed by examining the n.m.r. spectra of model compounds with known probable conformation. In condensed hydrocarbons containing carbonyl substituents the behaviour found may be substantially related to three distinct situations, those comparable to the α- and β-positions of naphthalene and overcrowded positions comparable to position 4 in phenanthrene. Calculation of the conformation behaviour by the semi-empirical methods provide qualitative correct results only for systems where steric interactions are small.

THE barriers preventing rotation around carbon–carbon bonds in aromatic aldehydes and ketones have been the subject of several studies on both the experimental determination of energy barriers and relative conformer stability and the theoretical interpretation of the physical findings.

We have already reported a survey [1] of the practical applicability and the relative criticism of MO semi-empirical and *ab initio* methods in the prediction of energy barriers and relative isomer stability in conjugated aldehydes and acetyl derivatives.

Experimental results can be obtained from different techniques such as Kerr molecular constants,[2,3] ^{1}H and ^{13}C n.m.r.,[4-6] u.v. spectroscopy,[7] and dipole moment measurements.[8,9] N.m.r. variable temperature studies may provide the energy barriers and the relative isomer populations, while this latter information is often obtained in aldehydes by also examining the long-range proton–proton coupling constant between the aldehyde proton and one of the protons of the attached ring, provided that the value for at least one isomer is known.

The lanthanide induced shift (LIS) has also been widely employed [10,11] for the conformational analysis of several organic compounds [12-16] and the relative isomer population determined is comparable with those obtained from other techniques.[17] The application of LIS is a reliable method in several cases for determining the relative isomer population in conditions of fast rotation, relative to the n.m.r. time scale, and affords information for variable temperature studies in order to determine energy barriers, since in the case of very unequally populated sites the dynamic n.m.r. technique requires special handling.[18] The use of lanthanide ions for conformational analysis is based on the assumption that complexation does not change the relative population of interchanging isomers and their molecular conformation remains unchanged: this point can be cleared up by a preliminary investigation carried out on a given substrate and by following a known experimental procedure.[19]

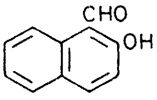
The present investigation reports the conformational results relative to a number of aldehydes and acetyl derivatives of condensed hydrocarbons by employing the LIS method. The results are compared with other conclusions drawn from the analysis of n.m.r. parameters, long-range proton–proton coupling constants, or chemical shifts. Tests of predictions based on the semi-empirical MO method PCILO [20] are also carried out. The reliability of this method in the analysis of the conformational behaviour of carbonyl compounds was previously tested: [1] qualitatively correct results were obtained for large classes of compounds, while it is applicable to large molecules where the employment of *ab initio* procedures is rather problematical.

EXPERIMENTAL

The ^{1}H n.m.r. spectra of the compounds in deuteriochloroform (0.3M) with tetramethylsilane as internal standard were recorded at 60 MHz on a JEOL C60 HL spectrometer. The reagent shift employed is Eu(fod)$_3$ added in known amounts to the solutions of the substrate examined. The experimental results were elaborated according to the procedures reported by Montaudo and his co-workers.[15]

The compounds (1)—(6) and (8)—(13) were commercial products purified according to known procedures. Phenanthrene-4-carbaldehyde (7),[21] 4-acetylphenanthrene (14),[22] 2-hydroxynaphthalene-1-carbaldehyde (15),[23] 1-hydroxynaphthalene-2-carbaldehyde (16),[23] and 3,4-dihydrophenanthren-1(2*H*)one (17) [24] were prepared according to literature methods.

Calculations were performed on a Cyber 76 CDC computer equipped with a plotting unit.



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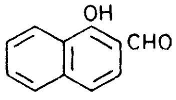

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RESULTS AND DISCUSSION

For the LIS analysis the McConnell and Robertson equation [25] was employed, by assuming that the interaction between lanthanide and substrate is entirely or predominantly of a pseudocontact nature. This has been verified [26] for ^{1}H n.m.r. spectra and the contact interaction was found to be significant only for protons directly bonded to the protonation site. Further, according to a previous report,[15] equimolecular lanthanide–substrate complexes (1 : 1) were considered to have axial symmetry and a constant geometry, as regards bond distances and bond angles, was maintained in the different conformers.

For determining the population ratio expression (1) was employed, where G_{1i} and G_{2i} are, according to

$$\Delta\delta_i = K(\chi_1 G_{1i} + \chi_2 G_{2i}) \qquad (1)$$

Montaudo and his co-workers,[15] the geometrical factors corresponding to two conformers, χ their molar fractions, and $\Delta\delta_i$ the LIS corresponding to the ith spectral signal. The geometry of the complex is simulated by assuming that the lanthanide atom is located at the oxygen atom of the carbonyl group, which is thus defined by the three geometrical factors,[15] R, ω, and ϕ. Following a common assumption,[27] to the R parameter for the Eu atom is constantly assigned a value of 3 Å. For solving the problem of determining conformer populations, in the case of a two-site exchange, four parameters have to be determined, *i.e.* ω, ϕ, K, and one of the χ values; thus at least four different $\Delta\delta_i$ values have to be employed.

In the computer simulation of the LIS proton spectra [15] for the best geometry of the complex the Hamilton agreement factor (AF) never exceeded 0.05. Molecular geometries were constructed from those of the parent hydrocarbons: [28,29] for the aldehyde and acetyl group the following bond distances were taken, C=O 1.22, C–H 1.085, C–CH_3, 1.515, Ar–C 1.485 Å; the bond angles were chosen to be perfectly trigonal. The aldehyde proton was not included in the simulation of LIS spectra since, being very close to the complexation site, it undergoes a contact shift which may introduce an error in the determination of conformer populations. The experimental LIS values may be simulated, either by introducing only the two rapidly equilibrating planar forms, or by taking into account the conformation obtained by rotating the aldehyde or acetyl group around the Ar–C bond of an angle θ which gives the best agreement between calculated and experimental values. It is thus often found that a predominant non-planar form reproduces better or to the same extent the experimental LIS values with respect to the situation of two planar forms both populated at the equilibrium: this fact may correspond to an artefact in the calculation of the AF values, but the presence of a non-planar highly populated conformation may well represent in certain molecules a physical identity.[15] The relative conformer populations for the derivatives investigated are reported in the Table. Discrimination between one single highly populated non-planar conformation and two planar forms both populated at equilibrium is rather problematical on the basis of the LIS technique, if not supported by supplementary experimental information. For example, in the case of *o*-methylbenzaldehyde the low temperature measurements allow us to discard the hypothesis of a single distorted conformer: LIS simulation for the situation of two planar conformers at equilibrium gives a E:Z ratio of 1.33 very close to the value which can be extrapolated from the low temperature determination recently reported.[30-32]

In naphthalene-1-carbaldehyde (2), 4-methoxynaphthalene-1-carbaldehyde (3), and 1-acetylnaphthalene (9) the results show that the Z-conformer is predominant as has been reported before.[6] This finding is explained both on the basis of mesomeric effects related to the particular *trans*-arrangement of the C=O and C(1)–C(2) bond [5] and to the fact [33] that the conformation with the carbonyl group pointing toward the neighbouring ring may be stabilized by a hydrogen-bond type interaction with the *peri*-hydrogen. Apart from the cause of the stability of this conformer, the same situation is found in the derivatives of phenanthrene substituted in position 9 with a formyl or acetyl group. This position may be compared, in fact, with position 1 of naphthalene [even the bond distance C(9)–C(10) of phenanthrene compares with C(1)–C(2) of naphthalene] and the same effects should operate in stabilizing the conformers of both compounds. In the case of the derivatives of phenanthrene substituted at the 2- or 3-position, the conformation of the acetyl group indicates that the ratio of E- and Z-isomers is close to unity: this fact is expected on the basis of the C–C bond distances [29] of the ring which, in this part of the phenanthrene molecule, are very close to each other. In 4-formyl- and 4-acetyl-phenanthrene the E-conformer is predominant, nearly 100%, and this is in agreement with the steric hindrance to which substituents in this position are subjected. For the formyl group it is the hydrogen atom that points towards the neighbouring rings, while in the acetyl derivative the oxygen atom occupies this position and the conformation is probably distorted by 30° from the molecular plane.

Finally for anthracene-9-carbaldehyde the results are not conclusive in distinguishing between the situation represented by equal amounts of two identical planar conformers at equilibrium and that of one 90° distorted conformation: from chemical shift values the first situation seems to be the most probable.

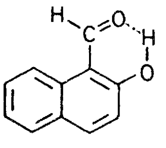
In a number of derivatives investigated here information on the conformer situation of the formyl group may be also obtained by examining the long-range proton–proton coupling constants over five bonds, ${}^5J_{H-CHO}$, *i.e.* between the formyl proton and the *meta*-proton of the ring. Calculations of rotamer populations from long-range coupling constants should be treated only from a qualitative point of view, since the experimental error which affects these values (±0.1 Hz in our measurements) is large compared with their values. In 2-hydroxynaphthalene-1-carbaldehyde the preferred conformation of the carbonyl group should be that corresponding to the E-conformer, owing to the intramolecular hydrogen bond, and ${}^5J_{H-CHO}$ is 0.46 Hz, while in 1-hydroxynaphthalene-2-carbaldehyde where the Z-conformer should be predominant, ${}^5J_{H-CHO}$ was not observed. In naphthalene-1-carbaldehyde, its 4-methoxy-derivative, and phenanthrene-9-carbaldehyde this coupling constant is not observed and it is probably

Experimental and calculated (in parentheses) LIS values,[a] molecular geometry parameters of the complexes, and relative amounts of conformational isomers in formyl and acetyl derivatives of condensed hydrocarbons

No.	Compound	1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-H	CH_3	CHO	*K*	ϕ(°)	ω(°)	AF	LIS method		Other methods	
																		E	*Z*	*E*	*Z*
(1)	2-Methylbenzaldehyde			3.93 (3.90)	3.28 (3.21)	4.17 (4.26)	11.62 (11.62)					8.33 (8.34)	17.04	1 196.54	35	10	0.0076	62	38	64 [b] 50 [c] 47 [d] 54 [d]	36 [b] 50 [c] 53 [d] 46 [d]
(2)	Naphthalene-1-carbaldehyde		6.33 (6.36)	2.93 (2.83)	2.63 (2.63)	2.45 (2.46)	2.19	2.71	16.57 (16.57)				15.75	1 050.32	15	0	0.0056	23	77	10 [e]	90 [e]
(3)	4-Methoxynaphthalene-1-carbaldehyde		6.46 (6.57)	3.10 (2.97)		2.78 (2.28)	2.30 (1.92)	2.73 (3.05)	18.90 (18.93)			2.19	16.02	961.74	40	0	0.0351	17	83	5 [e]	95 [e]
(4)	Naphthalene-2-carbaldehyde	7.02 (7.00)		12.56 (12.55)	3.70 (3.80)	2.07 (1.91)	1.33 (1.24)	1.37 (1.27)	2.08 (2.27)				18.60	1 073.49	35	40	0.019	86	14	80 [e]	20
(5)	Phenanthrene-9-carbaldehyde	2.1 (1.72)			2.6 (1.9)	2.6 (2.3)				16.1 (16.17)	5.8 (6.03)		15.76	1 017.65	10	0	0.049	75	25		
(6)	Anthracene-9-carbaldehyde	10.60 (10.61)	1.62 (1.63)	1.39 (1.50)	2.22 (2.10)						2.71 (2.68)		13.93	1 235.67	0	10	0.014	50	50		
(7)	Phenanthrene-4-carbaldehyde	2.10 (2.08)	2.60 (2.59)	12.38 (12.39)		7.50 (7.50)							14.92	911.48	75	20	0.0017	100	0		
(8)	*o*-Methylacetophenone			3.82 (3.79)	2.60 (2.80)	3.56 (3.33)	7.88					10.04 (10.04)	10.87	1 035.55	40	0	0.021	30	70	16 [d] 21 [d]	84 [d] 79 [d]
(9)	1-Acetylnaphthalene		7.10 (7.10)	2.90 (2.90)	2.50 (2.50)	2.20 (2.21)	2.30	2.50	15.30			12.70		1 006.98	20	20	0.00095	31	69		
(10)	2-Acetylnaphthalene	10.10 (10.11)		13.10 (13.08)	3.20 (3.46)	2.50 (1.88)	1.1	1.1	2.5 (2.65)			14.54		1 187.62	75	10	0.039	69	31		
(11)	3-Acetylphenanthrene	2.86 (2.79)	10.64 (10.66)		10.56 (10.54)	2.40 (2.45)						12.65		1 448.37	0	50	0.00613	50	50		
(12)	9-Acetylphenanthrene	1.88 (1.92)			1.84 (1.69)	1.84 (2.01)			13.47 (13.46)		6.33 (6.34)	11.06		898.22	15	0	0.01525	66	34		
(13)	2-Acetylphenanthrene	10.28 (10.28)		11.60 (11.59)	3.20 (3.31)	1.76 (1.60)						13.39		1 113.58	75	0	0.01208	57	43		
(14)	4-Acetylphenanthrene	1.94 (1.90)	1.89	9.50 (9.54)		8.46 (8.46)				1.52 (1.26)	1.52	9.23		739.32	60	0	0.02	100 [f]			

[a] Only clearly detectable signals were employed in the LIS analysis. [b] Ref. 30: from dynamic n.m.r. measurements; if the *E* : *Z* conformer ratio is extrapolated to 298 K, it is found to be 57 : 43. [c] Ref. 31: from dynamic n.m.r. measurements. [d] Ref. 32; populations evaluated from LIS data, by assuming distorted conformers: for 2-methylbenzaldehyde *E* (30.45°) and *Z* (30.30°), for 2-methylacetophenone *E* (45.60°) and *Z* (30.30°). [e] Ref. 5: from dynamic n.m.r. measurements. [f] Better fit is obtained for the *E*-conformer 30° distorted from planarity.

very near to zero: this is in agreement with the result of LIS measurements which indicates the *Z*-conformer as predominant, whereas it is not proved whether the conformation is completely planar. In naphthalene-2-carbaldehyde $^5J_{\mathrm{H-CHO}}$ amounts to 0.37 Hz, which, compared with the value of 0.46 Hz taken as the coupling



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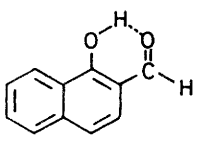

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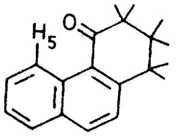
constant for the *E*-conformer, shows that this should be the predominant conformer, as obtained from LIS measurements. Examination of long-range coupling constants in phenanthrene-4-carbaldehyde also confirms the results obtained from LIS measurements, since the experimental value of 0.54 Hz for $^5J_{\mathrm{H-CHO}}$ indicates that the conformer having the carbonyl group pointing toward the neighbouring ring is predominant.

Even from the analysis of chemical shifts, information may be derived concerning the conformer population of carbonyl compounds, and this is especially so for 1-acetyl- or 1-formyl-naphthalenes by comparing the chemical shift of 8-H, which at δ 8.33 in 2-hydroxynaphthalene-1-carbaldehyde should correspond to the *E*-conformer, with the analogous position, 5-H, in compound (17) which

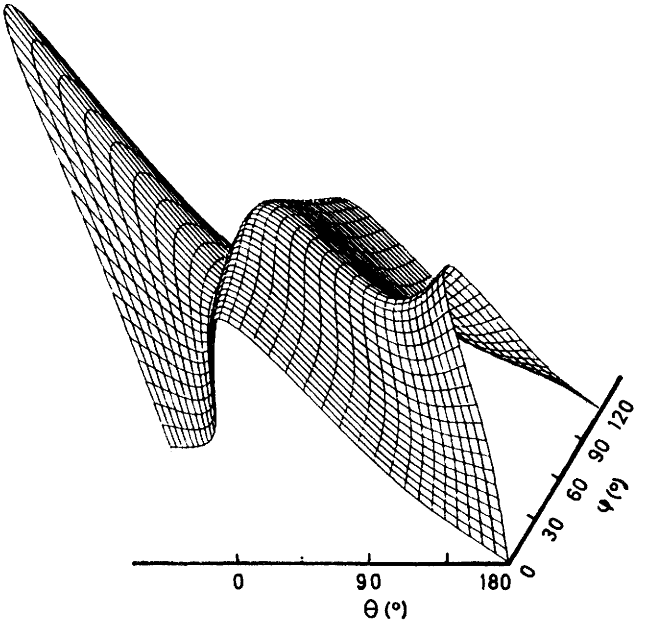


(17)

should correspond to the shift of the *peri*-proton in the *Z*-conformer and is δ 9.51. From the chemical shift of 8-H in naphthalene-2-carbaldehyde, corresponding to δ 9.221, the *E*-conformer in this molecule should amount to 25%; assuming that the most stable situation of the molecule is represented by the two rapidly equilibrating planar conformations, in agreement with the results from LIS measurements. If one assumes that only one conformation is present, of the *Z*-type, but with the carbonyl group slightly distorted from the molecular plane, by approximate calculations,[34] considering the ratio between the shift of 5-H produced in compound (17) and that for naphthalene-1-carbaldehyde, the angle of twist may be estimated as 22°. Accordingly, one may look for the best fit in LIS simulation for a non-planar conformation and this is found to be of *Z*-type with a twist angle of 45°. The agreement among the two estimates for a non-planar conformation is not satisfactory and we believe that the equilibrium between the two planar forms better describes the real molecular situation.

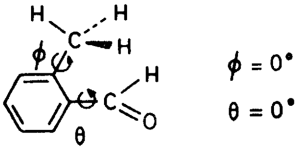
In the case of anthracene-9-carbaldehyde the chemical shift of 1-H measured in 0.5M-$CDCl_3$ solution is δ 8.87: on the basis of comparison of this value with the chemical shifts of the corresponding proton in the *Z*- and *E*-forms of naphthalene according to the estimates above reported, the two planar forms should be present in nearly the same amounts. Conversely, for 9-acetylanthracene, the chemical shift of 1-H is δ 7.93, close to that of the unsubstituted hydrocarbon, which should better correspond to a conformation largely distorted from planarity.

Energy Calculations.—When employing the semi-empirical MO method PCILO,[20] which we have previously tested [1] in the conformational analysis of carbonyl compounds, the energy minima for naphthalene-1-carbaldehyde do not correspond to planar conformations, even if a *Z*-type conformation distorted 30° from planarity is indicated as most populated. For naphthalene-2-carbaldehyde the energy behaviour reproduces qualitatively the experimental findings, even if the value derived, 9.10 kJ mol^{-1}, is rather smaller than that found experimentally,[6] 34.3 kJ mol^{-1} ($E \longrightarrow Z$). This should reflect the fact that semi-empirical methods underestimate bonding contributions between orbitals with respect to repulsive terms, thus steric effects are enhanced: this was shown [1] in the case of the CNDO/2 method and is probably also true for the PCILO method, even if to a smaller extent. For 1-acetyl- and 2-acetyl-naphthalene the minimum calculated by PCILO corresponds to the perpendicular and planar forms respectively, determined in the minimum energy conformation for the methyl group. For 2-acetylnaphthalene the *E*-conformer is estimated as more stable (*ca.* 80%) as in naphthalene-2-carbaldehyde, while the energy barrier turns out to be smaller.



Total energy calculated by the *ab initio* STO-3G MO approach for *o*-methylbenzaldehyde as a function of the angle θ and φ of rotation of the methyl and carbonyl groups around the exocyclic C–C bonds

To check the performances of the PCILO method for analysing the conformational behaviour of carbonyl compounds with respect to the presence of relevant steric effects, in certain molecules, we have compared the results of energy calculations by the PCILO and *ab initio* STO-3G [35] methods for *o*-methylbenzaldehyde: *ab initio* methods were shown to provide [1] the best estimates of conformational behaviour of carbonyl compounds with respect to semi-empirical methods, even when employed in the minimal basis set. Both methods show that the planar forms correspond to minima in the two dimensional energy diagram as a function of ϕ and θ angles. The PCILO method indicates the *Z*-conformer as more stable with an energy barrier of 9.18 kJ mol^{-1}, while from ***ab initio*** STO-3G the *E*-conformer is found to be the more stable and the energy barrier is 20.81 kJ mol^{-1}: experimentally [30] the *E*-conformer is more stable and the free energy of activation is 28.62 kJ mol^{-1}. The energy profile for the STO-3G calculation is reproduced in the Figure.



From these calculations, therefore, we find that in carbonyl derivatives where steric effects are small, as in derivatives of single-ring aromatic compounds not bearing *ortho*-substituents or in the positions of condensed hydrocarbons not equivalent to the α-sites of naphthalene, the PCILO method can correctly predict the energy of the conformational path and the relative energy of conformers, while for molecules containing groups or particular positions hindering the rotation of carbonyl substituents only by *ab initio* methods can a correct description of the conformational behaviour be obtained. This is a serious limitation for the analysis of large molecules where the application of *ab initio* methods becomes rather problematical.

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