Correlations Between Carbonyl Vibrational Properties of Polycyclic Aromatic Aldehydes and Electronic Properties of the Corresponding Hydrocarbons

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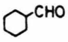
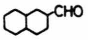
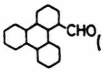
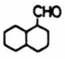
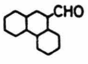
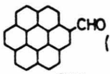
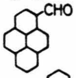
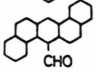
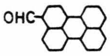
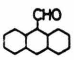
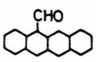
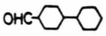
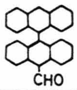
Good correlations exist between both the carbonyl stretching frequency and the carbonyl bond order of the monoaldehydes of polycyclic aromatic hydrocarbons and the HMO atom localisation energies or PMO reactivity numbers of the corresponding hydrocarbons at the carbon centres contiguous to the CHO group. Applications of these correlations are discussed.

The HMO atom localisation energy L_r [1] as well as the PMO reactivity number N_r [2] are suitable measures for the electronic donor properties of the centre r of a polycyclic aromatic hydrocarbon (PAH). However, these parameters have so far not been applied to find correlations with the properties of substituents in derivated PAH. Thus, the present work aims at gaining information whether and to what extent L_r and N_r values of unsubstituted PAH correlate with the bond order ϱ_{CO} and the carbonyl stretching frequency ν_{CO} of simple carbonyl derivatives of PAH. In principle, both parameters are known to be very sensitive to mesomeric effects [3].

Accordingly, we have studied the ir spectra of benzaldehyde and the monoaldehydes of 12 PAH under identical conditions. In this context it is important to note that the mass influence of the molecular unit linked to the CO group on ν_{CO} can be neglected for masses above ca 50 as follows from the mechanical model of the stretching vibration [4]. Furthermore, inspection of Stuart-Briegleb models of the compounds studied shows that steric hindrance between the CHO group and the aromatic unit is negligibly. Thus, the presumptions for a purely mesomeric effect in these systems appear to be warranted.

The compounds studied are listed in Table 1. Aldehydes **1**, **2**, **4**, **5**, **7** and **10** were commercial samples (EGA Chemie GmbH & Co KG, Steinheim), all remaining compounds were synthesized by the Rieche method [5, 6] using a standard procedure which will be described elsewhere [7]. The aldehydes were purified by crystallisation and chromatography and their purity assured by determination of the melting points, elemental analysis, ir, uv, ^{1}H nmr and mass spectra and also by high pressure liquid chromatography. Aldehydes **3**, **8** and

Table 1
Experimental and theoretical data of polycyclic aromatic aldehydes and the corresponding hydrocarbons

	ρ_{CO}	N_r [β]	L_r [β]	$\tilde{\nu}_{CO}$ [cm^{-1}]
 (1)	0.7824	2.31	2.54	1708.9
 (2)	0.7774	2.12	2.48	1700.7
 (3)	0.7694	2.00	2.38	1702.2
 (4)	0.7613	1.81	2.30	1698.3
 (5)	0.7611	1.80	2.30	1698.3
 (6)	0.7621	1.80	2.31	1697.8
 (7)	0.7485	1.51	2.19	1696.5
 (8)	0.7437	1.51	2.13	1696.4
 (9)	0.7418	1.33	2.14	1686.3
 (10)	0.7269	1.26	2.11	1683.1
 (11)	0.7125	1.03	1.93	1677.5
 (12)	—	—	—	1707.0
 (13)	—	—	—	1683.6

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* Part of the thesis C. Lohberger, Clausthal-Zellerfeld 1981. Adresses of authors: Prof. Dr. K. D. Gundermann, Organisch-Chemisches Institut der TU Clausthal, Leibnizstr. 6, D-3392 Clausthal-Zellerfeld. Dipl.-Chem. C. Lohberger, Prof. Dr. M. Zander, Rütgerswerke AG, Kekuléstr. 30, D-4620 Castrop-Rauxel.

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13 have not yet been described in the literature and their constitutions have been proven by the same methods. A full description of their synthesis and properties will be given elsewhere [7].

A Perkin-Elmer 283 B spectrometer was used for the ir measurements. All spectra were recorded in CS_2 solution at room temperature (concentration: 2.5 mg/ml, cell length: 0.5 mm, registration speed: 5.5 s/cm^{-1}). All samples have been measured at least three times and the experimental error of the ir measurements was estimated as less as 1 cm^{-1}.

Table 1 gives a compilation of the compounds studied, their CO stretching wave numbers $\tilde{\nu}_{CO}$ (cm^{-1}), the L_r and N_r values (in β units) [1, 2] of the carbon centres r to which the CO group is bound and finally the HMO bond orders ϱ_{CO} of the CO group. For the calculation of ϱ_{CO} the Zahradnik parametrisation was used [8].

In Fig. 1 the experimental $\tilde{\nu}_{CO}$ data are plotted versus the respective L_r or N_r values for the aldehydes **1**—**11**. Good correlations are observed and the least squares lines are represented by

$$\tilde{\nu}_{CO} = 47\,L_r + 1589 \quad (\text{cm}^{-1}) \tag{1}$$

(correlation coefficient: 0.910),

$$\tilde{\nu}_{CO} = 22\,N_r + 1658 \quad (\text{cm}^{-1}) \tag{2}$$

(correlation coefficient: 0.945).

The N_r values, which can be calculated extremely easily even for systems containing a very large number of carbon centres [2], correlate slightly better with the experimental data than the L_r values.

A detailed analysis [9] indicates that the force constant for a bond is a function of both the bond order ϱ and the bond polarizability, but for a class of compounds the use of ϱ alone suffices for satisfactory correlations. Accordingly, parabolic correlations exist between ϱ_{CO} and L_r or N_r, respectively, for the compounds studied (Figure 2). The best fits, obtained by regression analysis, are given by

$$\varrho_{CO} = -\,0.064\,(L_r - 3.16)^2 + 0.808 \tag{3}$$

(correlation coefficient: — 0.986),

$$\varrho_{CO} = -\,0.018\,(N_r - 3.12)^2 + 0.794 \tag{4}$$

(correlation coefficient: — 0.991).

Equation (4) provides a very simple means for

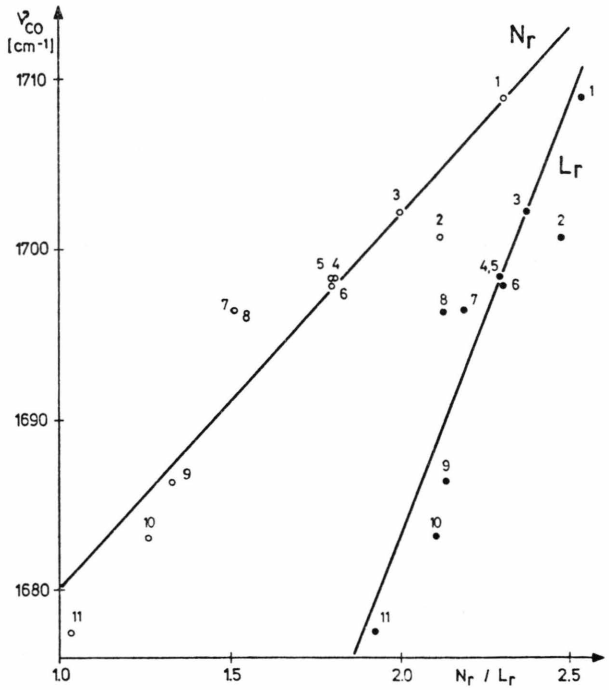

Fig. 1. $\tilde{\nu}_{CO}$ (cm^{-1}) of aromatic aldehydes as functions of atom localisation energy $L_r(\beta)$ or reactivity number $N_r(\beta)$, respectively, of centre r of the corresponding hydrocarbons.

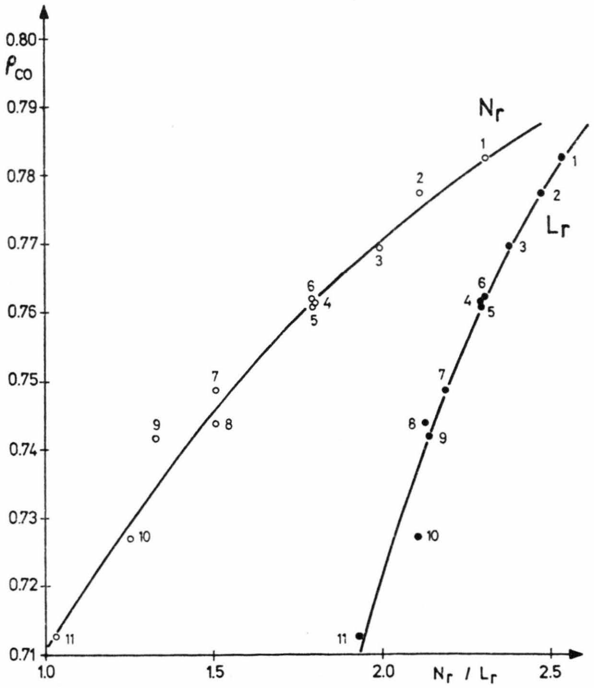

Fig. 2. Correlations of CO bond order ϱ_{CO} of aromatic aldehydes and L_r and N_r, respectively, of the corresponding hydrocarbons.

estimating CO bond orders of aromatic aldehydes from the N_r values of the unsubstituted hydrocarbons.

Since the lowest N_r value ($N_{r(\mathrm{min})}$) of a given alternant PAH is related to the first ionisation potential of the hydrocarbon, and consequently to the energy of the HOMO ($\varepsilon_{\mathrm{HOMO}}$) [10] a correlation also exists between $\varepsilon_{\mathrm{HOMO}}$ of the unsubstituted hydrocarbons and $\tilde{\nu}_{\mathrm{CO}}$ of those aldehydes where the CO group is bound to the carbon centre r_{min}.

Equation (2) can be used for the structure determination of aromatic aldehydes. Provided the structure of the aromatic system is known, for example from uv and mass spectra of the aldehyde, the position of the CHO group can be found by calculating the corresponding N_r value from $\tilde{\nu}_{\mathrm{CO}}$ and comparison with the relevant N_r values of the system. Clearly, unambiguous results are only obtainable for sufficiently differing N_r values.

We have also included in our study biphenyl-4-aldehyde (**12**) and 9,9′-bianthryl-10-aldehyde (**13**) (Table 1). The carbonyl stretching frequencies of these aldehydes are very similar to those of benzaldehyde or anthracene-9-aldehyde (**10**) respectively. This is in accordance with the non-planarity of **12** and **13**. In these cases the calculated data, used in the present study, cannot be applied as they are meaningful only for planar π-electronic systems.

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