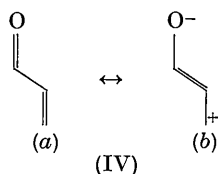


Nous voudrions faire remarquer que l'hypothèse sur la grande polarité est incompatible avec l'observation sur la longueur exceptionnellement courte de liaisons en question. En effet, rien qu'en utilisant la représentation courante de la théorie de la mésomérie on peut voir aisément qu'une forte polarité des carbonyles et en particulier une forte accumulation des charges électroniques sur leurs oxygènes résulte dans les molécules conjuguées d'une grande importance des formules ioniques du type (IVb) qui, nécessairement, représentent la liaison carbonyle comme simple, donc longue. Une liaison CO courte ne saurait être très polaire.



Cet état de choses est précisé par l'examen de la distribution de charges électroniques et des indices de liaison mobile dans les composés intéressés. Prenons à titre d'exemple le cas de l'alloxane. Selon les résultats expérimentaux, le contact rapproché a lieu entre O(6) et C(5). La distribution de charges électroniques dans cette molécule, évaluée par la méthode des orbitales moléculaires (Pullman & Pullman, 1963) est représentée par la Fig. 1. On constate que les groupes carbonyles engagés dans ce contact ne sont nullement les groupes les plus polaires de la molécule. Leur polarité est plus faible que celle du groupe C(2)-O(2). Il en est ainsi essentiellement en ce qui concerne la charge négative nette de l'oxygène. La charge positive nette du C(5) est effectivement plus élevée que celle des autres groupes carbonyles de la molécule.

En revanche, les liaisons carbonyles impliquées dans le contact rapproché ont un indice de liaison mobile particulièrement élevé (Fig. 2). En fait cet indice décroît tout à fait parallèlement à l'élongation des différentes liaisons carbonyles de l'alloxane.

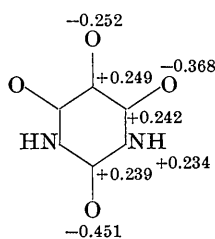


Fig. 1. Charges électroniques nettes dans l'alloxane.

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A dynamic effect in electron diffraction by molecules. By JON GJØNNES, *Department of Physics, University of Oslo, Norway**

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Dynamic scattering within the atoms has been known for some time to contribute to the electron diffraction

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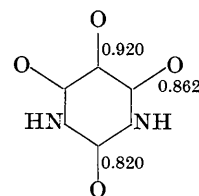


Fig. 2. Indices mobiles de liaisons CO dans l'alloxane.

Le caractère général de cette situation est illustré dans le Tableau 1 qui compare les charges et les indices mobiles des liaisons carbonyles de (I), (II) et (III) qui sont impliqués dans des contacts rapprochés avec des liaisons analogues d'autres purines et pyrimidines d'intérêt biologique.

Tableau 1. *Caractéristiques des liaisons CO* (Pullman & Pullman, 1963)

Composé	Indice mobile	Charge nette du C	Charge nette du O
Acide barbiturique	0,864*	+0,252*	-0,393*
	0,819	+0,239	-0,454
Acide parabanique	0,864*	+0,242*	-0,364*
	0,822	+0,239	-0,447
Cytosine	0,778	+0,204	-0,492
Uracil	0,799	+0,212	-0,456
	0,811	+0,232	-0,463
Acide orotique	0,801	+0,213	-0,452
	0,810	+0,232	-0,464
Guanine	0,796	+0,207	-0,461
Acide urique	0,790	+0,202	-0,467
	0,806	+0,228	-0,469
	0,776	+0,201	-0,499

* Liaisons CO engagées dans les contacts rapprochés.

Il résulte de ce tableau que les liaisons carbonyles impliquées dans les contacts rapprochés sont caractérisées par un indice mobile particulièrement élevé, une charge nette positive sur le carbone impliqué dans le contact également très élevée mais, en revanche, par une charge nette négative relativement très faible sur leur oxygène.

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formulae of the kinematic theory. These dynamic scattering factors may also include dynamic interactions by inelastic processes (Gjønnnes, 1962).

The question whether dynamic interactions involving different atoms in a molecule may be of importance in electron diffraction by gases was first raised by Hoerni (1956) who concluded from calculations relating to a diatomic molecule that only a small contribution to the background was expected.

The purpose of this note is to point out, on the basis of some calculations performed a few years ago, relating to the P_4 molecule, that dynamic scattering may be significant in electron diffraction from gas molecules containing three or more heavy atoms. The nature of the contribution can be seen through a simple argument: The left ray path in Fig. 1 symbolizes multiple scattering† by the atoms i and j . Since the scattering is strongly peaked in the forward direction, this double scattering will give an appreciable contribution only when the molecule has the orientation shown, *i.e.* when the vector \mathbf{r}_{ij} is nearly parallel to the incident beam. The phase difference between this ray path and the right path representing single scattering by atom k is approximately $\exp(i\mathbf{s}\rho)$, where ρ is the normal from k to the line joining i and j , and \mathbf{s} is the scattering vector. On averaging over the contributing orientations a Bessel function, $J_0(s\rho)$ results. Hence this 'triangular multiple scattering term', which can be schematically written $F_{i \rightarrow j} \times F_k^*$, will be the product of the scattering factor for the atom at k and a scattering factor relating to the two overlapping atoms i and j .

The scattering amplitude, $F_{i \rightarrow j}$, corresponding to the left path in Fig. 1 can be obtained from the corresponding

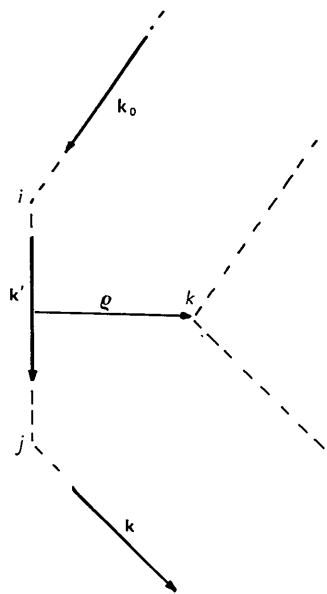


Fig. 1. Schematic representation of 'triangular scattering term'. Centre of atoms at i , j and k .

† 'Multiple scattering' used in the sense of Hoerni (1956) and Fujiwara (1959).

term in the Born series expansion, as shown by Hoerni (1956):

$$F_{i \rightarrow j} = (\frac{1}{2}\pi a_H) \int \exp(i\mathbf{k}\mathbf{r}') U_j(\mathbf{r}' - \mathbf{R}_j) \psi_i(\mathbf{r}') d\mathbf{r}' \quad (1)$$

where a_H is the Bohr radius for hydrogen, U_j is the potential distribution around the j th atom and ψ_i is the amplitude of the wave scattered by the i th atom. In a recent paper Bunyan (1964) has given a thorough discussion of the resulting expression and also studied other types of higher order terms; here we shall only give the form of the intensity term corresponding to Fig. 1 after averaging over all orientations of the molecule. The rotation around \mathbf{k}' results essentially in a Bessel function as anticipated; the remaining integration over all directions of \mathbf{k}' can be written as a convolution integral on the Ewald sphere:

$$F_{i \rightarrow j} F_k^* \simeq (2/a_H) R_{ij}^{-1} J_0(s\rho) f_k(s) \int f_i(\mathbf{s}_1) \times \exp(i\frac{1}{2}\mathbf{s}_1 \mathbf{R}_{ij}) f_j(\mathbf{s}_2) d\mathbf{f}_{\mathbf{k}'} \quad (2)$$

where \mathbf{s}_1 and \mathbf{s}_2 are the intermediate scattering vectors, \mathbf{R}_{ij} the vector between the atoms i and j (Fig. 1) and the atomic scattering factors f_i do not include $2/a_H$.

The convolution integral can be performed through expansion in spherical harmonics *or*, restricting calculations to small and intermediate angles ($s \leq 20$), by expansion in the zero-order Bessel function. In order to include all interactions within the atoms, the complex scattering factors $f_{i,j,k}$ should be used. By Bessel function expansion we calculated the triangular term for the P_4 molecule up to $s = 18$ at an electron energy of 36 keV. The amplitude of the Bessel function was found to be up to 5% of the amplitude of the $\sin sR/sR$ term. Attempts were made to compare the result with experimental intensity curves after subtraction of background and calculated kinematical molecular scattering. The fluctuations in the observed intensity curve were too large, however, to allow a clear demonstration of the triangular term.

Some conclusions can be drawn from the calculations, however. The magnitude of the triangular term will depend on the atomic numbers involved and on the multiplicity of the triangle. Assuming P_4 to be a borderline case, appreciable contribution from this type of dynamic scattering is to be expected in molecules like Cl_4 , As_4 , CBr_4 and CHI_3 , in that order.

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