Crystal data of 'three-pyraphene' and of some derivatives of 'dipyraphene'. By A. FERRARI, A. BRAIBANTI &
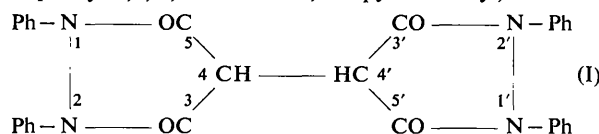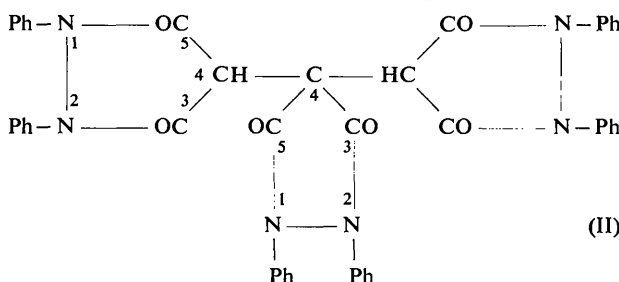
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The chemical constitution of 'dipyraphene' (1,2,1',2'-tetraphenyl-3,5,3',5'-tetraoxo-4,4'-dipyrazolidinyl)

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Ph – N ——— OC              CO ——— N – Ph
    |1          5\        /3'      2'|
    |                4 CH ——— HC 4'    |        (I)
    |2         3/        \5'      1'|
Ph – N ——— OC              CO ——— N – Ph
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and of 'three-pyraphene' (1,2-diphenyl-3,5-dioxo-4,4- bis-(1,2-diphenyl-3,5-dioxo-4-pyrazolidinyl) pyrazolidine)

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Ph – N ——— OC                        CO ——— N – Ph
    |1          5\                  /
    |                4 CH —— C —— HC              |
    |2         3/        /4\       \
Ph – N ——— OC     OC   CO         CO ——— N – Ph
                   5|   3|
                   |     |
                   |1    2|
                   N ——— N                      (II)
                   |     |
                   Ph    Ph
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has been determined by Cardani & co-workers (Cardani, Scaramuzza, Mondelli & Merlini, 1963; Mondelli, Merlini, Bovis & Cardani, 1964).

The dipotassium and disodium salts of compound (I) are very likely derived from the dienolic form of (I), 1,2,1',2'-tetraphenyl-3,3'-dienol-5,5'-dioxo-4,4'-dipyrazolidinyl.

The crystals of these compounds have been examined and the crystal data determined.

Compound (I). Dipyraphene, $C_{30}H_{22}N_4O_4$.
Crystal shape: Very fine needles, easily altered by light.

Compound (II). Three-pyraphene, $C_{45}H_{32}N_6O_6$.
Crystal shape: very fine needles; [001] parallel to the elongation axis.

Compound (III). Dipotassium dipyraphene, $C_{30}H_{20}N_4O_4K_2$.
Crystal shape: thick plates, monoclinic, [010] parallel to the longest edges.

Compound (IV). Disodium dipyraphene, $C_{30}H_{20}N_4O_4Na_2$.
Crystal shape: flat plates with rhomboidal faces; [010] parallel to the shorter diagonal of the basal rhomboid.

The unit-cell constants obtained with Cu $K\alpha$ radiation are shown in Table 1.

Table 1. *Crystal data*

Compound	II	III	IV
a	$14\cdot92 \pm 0\cdot01$	$16\cdot39 \pm 0\cdot01$	$14\cdot77 \pm 0\cdot01$ Å
b	$24\cdot80 \pm 0\cdot03$	$12\cdot36 \pm 0\cdot03$	$14\cdot28 \pm 0\cdot01$ Å
c	$12\cdot28 \pm 0\cdot01$	$15\cdot50 \pm 0\cdot01$	$15\cdot65 \pm 0\cdot01$ Å
β	$110° 46' \pm 18'$	$116° 22' \pm 11'$	$104° 25' \pm 14'$
U	4241	2818	3198 Å³
Space group	$P2_1/c$	$P2_1/a$	$P2_1/c$
Molecular units per unit cell	4	4	4
ϱ calc.	$1\cdot18$	$1\cdot37$	$1\cdot14$ g.cm⁻³

Crystals of compound (I) are altered very rapidly by light.

The crystals of the dipotassium and disodium salts of 'dipyraphene' are not isostructural.

In the photographs of these compounds, the reflexions become very weak at moderate values of θ owing to thermal motion.

The determination of the crystal structure of dipotassium dipyraphene is in progress.

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Improved approximation for incoherent X-ray scattering*. By S. E. RODRIGUEZ and C. J. PINGS, *Division of Chem-

istry and Chemical Engineering, California Institute of Technology, Pasadena, California, U.S.A.*

The incoherent or modified part of the X-ray intensity scattered by an atom, neglecting exchange terms, is given (James, 1958, p. 462) by

$$I_{inc} = Z - \sum_{1}^{z} f_K^2 \qquad (1)$$

where Z is the atomic number and f_K is the scattering factor corresponding to individual electronic wave functions. f_K is unity at zero angle of scatter and decays to oscillation about zero for increasing $\sin \theta / \lambda$.

Table 1. *Comparison of approximations for incoherent scattering*

sin θ/λ	f	I_{inc}*	I_{inc}†	I_{inc}(Eq. 3)	I_{inc}(Eq. 4)
		$Z=8$			
0	8[a]	0[b]	0[b]	0	0
0·2	5·630	3·700	2·797	4·038	2·370
0·4	3·008	5·811	5·271	6·869	4·992
0·7	1·714	6·542	6·417	7·633	6·286
1·1	1·294	7·130	7·036	7·791	6·706
		$Z=32$			
0	32[c]	0[b]	0[b]	0	0
0·2	25·09	8·61	4·75	13·33	6·91
0·4	18·53	16·73	10·02	21·28	13·47
0·7	11·34	22·47	16·59	27·98	20·66
1·1	7·24	25·52	21·90	30·36	24·76

* Without exchange terms.　† Including exchange terms.
[a] Freeman (1959a).　[b] Freeman (1959b).　[c] Berghuis *et al.* (1955).

James suggests that, lacking other information, the individual electronic factors may be replaced by $f_K = f/Z$, where

$$f = \sum_{1}^{z} f_K \tag{2}$$

is the total or atomic scattering factor. Thus, equation (1) becomes

$$I_{\text{inc}} = Z - f^2/Z , \tag{3}$$

a form which is used in practice (Furukawa, Orton, Hamor & Williams, 1963).

Equation (3) implies that all f_K contribute equally to f for all angles of scatter. However, electronic scattering factors are markedly affected by the spread of the electronic charge distribution (James, 1958, p. 125); the more concentrated the charge distribution, the more slowly will f_K decrease as sin θ/λ increases. Furthermore, once an f_K has fallen to zero, it never regains appreciable positive or negative values. Hence, the decline of the total factor f does not result from equal contribution from the various electronic wave functions. Rather, the f_K of outer electrons decay early to zero, while that from inner electrons falls off very slowly.

A better approximation would assign the entire decrease in atomic factor f to outer orbitals. For some number of outer electrons f_K is assumed to be zero, while the f_K of the remaining inner electrons stays at unity, the distribution being such as to satisfy equation (2). There follows that only a number f of electrons (generally a noninteger value) have the f_K of unity. and equation (1) gives

$$I_{\text{inc}} = Z - f . \tag{4}$$

This new approximation has a supplementary attraction in cases where exchange terms are important. Equations (3) and (4) give respectively the maximum and minimum physically possible values of equation (1). Since equation (1) already gives too large an estimate for I_{inc} because of neglect of exchange terms (James, 1958, p. 116), equation (4) has the right trend.

Because both equations (3) and (4) are merely plausible approximations, they should be judged by comparison with more reliable estimates of incoherent scatter. Equation (4) may be expected to work better for the elements of larger atomic number, which have both greater differences among the electronic f_K and more important exchange terms. Oxygen of relatively small $Z = 8$ and germanium with $Z = 32$ are taken as examples. Table 1 gives quantum-mechanical values of f and I_{inc} (without and including exchange terms) plus the approximate I_{inc} from equations (3) and (4) for some values of sin θ/λ.

The new approximation of equation (4) appears superior for both elements, even if exchange terms are excluded. For the light oxygen atom the minimizing effect of equation (4) is too large, and the estimated I_{inc} falls below the accurate value. By $Z = 32$ for germanium, the effect is already reversed, the actual I_{inc} being less than that given by either approximation. Thus, the new approximation is decidedly better for heavier elements, for which it is most often required.

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Elastische und thermoelastische Konstanten von Benzalazin, gemessen mit dem Schaefer–Bergmann-Verfahren.

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Vor kurzem teilten Joshi & Kashyap (1964) elastische Konstanten von Benzalazin mit, die sie aus der diffusen Streuung von Röntgenstrahlen in Anlehnung an ein schon früher von Wooster und Mitarbeiter benutztes Verfahren bestimmt hatten (siehe Wooster, 1962). Nach diesen Werten würde Benzalazin die höchste bisher bekannte elastische Anisotropie aufweisen ($c_{11} \simeq 8c_{22}$); ausserdem würde sich die in [100] schwingende reine Transversalwelle in Richtung [010]