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**Remarks on 'improved' atomic form factors.** By JAMES A. IBERS, *Shell Development Company, Emeryville, California, U.S.A.*

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Recently Hurst, Miller & Matsen (1958) (hereafter abbreviated HM&M) calculated atomic form factors for the two-electron systems  $H^{-1}$  through  $C^{+4}$  using the radial-correlated analytic wave functions of the Hylleraas-Eckart type with parameters of Shull & Löwdin (1956). HM&M note that these wave functions lead to lower total energies for the two-electron systems than do other approximations, and on this basis state that the form factors derived from Hylleraas-Eckart wave functions may represent an improvement on those based on self-consistent fields. A wave function is regarded as better than another within the framework of the variation principle if it leads to a lower energy for the whole atomic system. Experience has shown that the energy criterion is a generally useful one, but it is by no means true that a wave function yielding a lower energy is necessarily better than another in the sense of better representing the true wave function reliably over a large region of space. Thus, Bartlett (1955) has shown that there are serious defects in Hylleraas's best approximations for the helium atom in some regions of  $r$ . Moreover, Green *et al.* (1954) indicate that relatively good energies can be obtained from relatively poor wave functions. As a function of scattering angle the atomic form factor is a complicated function of the wave functions, and it does not follow, as HM&M imply, that those wave functions yielding the lowest energy will *a priori* yield the most reliable atomic form factors. In view of this, an important point, and one which HM&M failed to infer from their results, partly because of their rather unfortunate choice of James & Brindley (1931) form factors for comparison, is that the atomic form factors, even for the very light two-electron atoms and ions, are relatively insensitive to the wave functions used. Insensitivity, from the point of view of present experimental detectability, to radial correlation effects for the slightly heavier atom beryllium had already been established (Ibers, 1957), and a comparison of the radial correlated and uncorrelated (Slater wave function) results of

HM&M indicates that except, of course, for  $H^{-1}$ , this is true also for the two-electron systems. Of more interest is the direct comparison of the results of HM&M with Hartree-Fock calculations. Freeman (1958) has computed the atomic form factors for  $Li^+$  and for  $C^{+4}$  from the single-configuration Hartree-Fock wave functions of Fock & Petrashen (1935) and Jucys (1939), respectively. Freeman's results are in remarkable agreement with the radial-correlated results of HM&M, the maximum deviations being only 0.003 electrons for  $C^{+4}$  and 0.005 electrons for  $Li^+$ . Other comparisons can be made in the region  $\sin \theta/\lambda > 0.4$  of the results of HM&M with those for the neutral atoms Be and B (Ibers, 1957; Hartree-Fock, multiple configuration): here the agreement is within about 2%. Such excellent agreement is, of course, most fortunate, for insensitivity of atomic form factors of even the very light atoms to refinements in the calculations of atomic wave functions and to their reliability on an energy criterion, makes immensely simpler the task of obtaining reliable atomic form factors.

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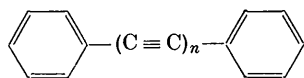
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**The crystal structures of  $\alpha$ ,  $\omega$ -diphenyl-poly-ynes. I. Crystal data.** By T. WATANABÉ, I. TAGUCHI and N. MASAKI, *Faculty of Science, Osaka University, Osaka, Japan*

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In order to elucidate the physical and chemical properties of substances having the conjugated triple bonds, it is of primary importance to determine the detailed molecular and crystal structure of compounds having these.

For this purpose, the series of  $\alpha, \omega$ -diphenyl-poly-ynes



was chosen, because homologous members with  $n =$

1, 2, 3, 4, 5, 6 and 8 are now available (Nakagawa, 1950a, 1950b; Jones *et al.*, 1951; Schlubach & Franzen, 1951; Nakagawa & Inui, 1952). While the crystal structure of tolane ( $n = 1$ ) has been reported by Robertson & Woodward (1938), and of diphenyl-diacetylene ( $n = 2$ ) by Wiebenga (1940), other members of the homologous series remained yet to be explored.

We have determined the unit-cell dimensions and space groups of these members with  $n = 3, 4$  and 5. Single crystals of  $\alpha, \omega$ -diphenyl-1,3,5-hexatriyne ( $n = 3$ ) were obtained from methanol solution.  $\alpha, \omega$ -diphenyl-1,3,5,7-

octatetrayne ( $n = 4$ ) was found to give two modifications which we shall call  $\alpha$  and  $\beta$ . Single crystals of the  $\alpha$  form were obtained from ethyl acetate solution, whereas those of the  $\beta$  form were obtained by rapid cooling of petroleum ether solution. Single crystals of  $\alpha, \omega$ -diphenyl-1,3,5,7,9-decapentayne ( $n = 5$ ) were obtained from petroleum ether solution. All these crystals are needles in shape. Triyne is slightly brown, and tetrayne and pentayne are yellow in color. They are photosensitive and seem to be less stable when  $n$  becomes higher.

Results are outlined in Table 1, where the values

Table 1. *Crystal data of  $\alpha, \omega$ -diphenyl-polyynes*

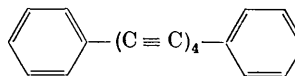
$n$	m.p. (°C.)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$	Space group	$Z$
1*	62.5	12.75	5.73	15.67	115.2°	$P2_1/a$	4
2†	86	14.92	6.04	6.61	105°	$P2_1/a$	2
3	95	23.3	7.04	20.3	125°	$P2_1/a$	8
4 $\alpha$	—	17.74	3.99	10.78	110.5°	$P2_1/a$	2
$\beta$	113	19.5	9.08	3.95	99°	$P2_1/a$	2
5	165	17.5	5.12	9.25	112°	$P2_1/a$	2

\* Robertson & Woodward (1938).

† Wiebenga (1940).

reported by Robertson & Woodward (1938) and by Wiebenga (1940) are also included for reference.

The structure of the  $\alpha$  form of  $\alpha, \omega$ -diphenyl-1,3,5,7-octatetrayne



has been determined using the intensity data collected at  $-110^\circ\text{C}$ . The detailed analyses of this modification and of the other members will be reported in later communications.

We express our hearty thanks to Prof. M. Nakagawa for providing the materials at our disposal.

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### Crystal data of two substituted nickel ethylenediamine complexes. By D. A. WRIGHT, *Chemistry Department, University of Auckland, New Zealand*

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It has been shown recently in this department (Curtis, 1954) that two, three or four molecules of acetone may be condensed on to a molecule of nickel ethylenediamine perchlorate ( $\text{Ni}(\text{C}_2\text{N}_2\text{H}_8)_2\text{ClO}_4$ ) to give three distinct stable products. These may be postulated as nickel-Schiff base complexes having imine linkages external to and coplanar with the ethylenediamine rings bonded to the nickel. All three products are diamagnetic both as solids and in solution, which shows them to have a planar square configuration of nickel bonds (Curtis, 1954). The two compounds having 3 and 4 acetone molecules condensed are expected to have steric hindrance of the methyl groups of the acetone residues, but may be stabilized by resonance effects in the latter case. When only 2 acetone molecules are condensed two possible configurations exist, the *trans* configuration being the most likely. A preliminary crystallographic investigation of those products with 2 and 4 molecules of acetone condensed on to the ethylenediamine rings has been made.

#### Nickel ethylenediaminetetraacetyl perchlorate:

Formula  $\text{C}_{16}\text{H}_{32}\text{N}_4\text{Ni}(\text{ClO}_4)_2$  or  $\text{Ni}2\text{en}4\text{ac}2\text{ClO}_4$  where  
 en = ethylenediamine residue  $\text{C}_2\text{N}_2\text{H}_4$ ,  
 ac = acetyl residue  $(\text{CH}_3)_2\text{C}$ .

Orthorhombic,

$$a = 19.7, \quad b = 16.9, \quad c = 13.6 \text{ \AA} \quad (\text{all } \pm 1\%)$$

$$(\text{Cu } K\alpha, \lambda = 1.542 \text{ \AA}).$$

Absent spectra:

$h0l$  when  $l \neq 2n$ ,  $0kl$  when  $k \neq 2n$ ,  $hk0$  when  $h \neq 2n$ .

Space group  $Pbca$ . Eight molecules per unit cell. Density (calc.)  $1.58 \text{ g.cm.}^{-3}$ , density (obs.) flotation  $1.57 \text{ g.cm.}^{-3}$ .

#### Nickel ethylenediaminediacetyl perchlorate:

Formula  $\text{C}_{10}\text{H}_{22}\text{N}_4\text{Ni}(\text{ClO}_4)_2$  or  $\text{Ni}2\text{en}2\text{ac}2\text{ClO}_4$ .

Monoclinic,

$$a = 14.3, \quad b = 12.5, \quad c = 10.3 \text{ \AA} \quad (\text{all } \pm 1\%),$$

$$(\text{Cu } K\alpha, \lambda = 1.542 \text{ \AA}),$$

$$\beta = 102^\circ 40' \text{ (found by measuring } d(101)).$$

Absent spectra:  $h0l$  when  $h \neq 2n$ ,  $0k0$  when  $k \neq 2n$ .

Space group  $P2_1/a$ . Four molecules per unit cell. Density (calc.)  $1.68 \text{ g.cm.}^{-3}$ , density (obs.) flotation  $1.68 \text{ g.cm.}^{-3}$ .

No further work is contemplated with these compounds.

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