

Finally, the free amino sugars and their N-acetyl derivatives synthesized chemically or enzymatically with enzymes from *E. coli* strain B, or isolated from *C. violaceum*, had identical mobilities on paper chromatography in five solvent systems.

As in the case of *E. coli* strain Y-10, the large amount of TDP-4-acetamido-4,6-dideoxy-D-glucose found in *E. coli* strain B is presumably a reflection of the inability of this strain to utilize the nucleotide for polysaccharide synthesis. *E. coli* strain B and *C. violaceum* (which contains viosamine in its lipopolysaccharide) are unusual in containing 4-amino-4,6-dideoxy-D-glucose, since 14 other strains of enteric bacteria which have been examined are able to synthesize only the sugar with D-galacto configuration.

Acknowledgment.—We acknowledge Grant No. GM 11520 of the National Institutes of Health, Division of General Medical Sciences, at Wayne State University; Grant No. AM 01158 of the National Institutes of Health and G 18742 of the National Science Foundation at Washington University and the University of Wisconsin; and Grant No. AM 07588-01 of the National Institutes of Health at Nagoya University.

(8) National Science Foundation Predoctoral Fellow.

(9) National Institutes of Health Postdoctoral Fellow.

DEPARTMENT OF CHEMISTRY WAYNE STATE UNIVERSITY DETROIT, MICHIGAN	CALVIN L. STEVENS PETER BLUMBERGS FRANCIS A. DANIHER ⁸
DEPARTMENTS OF PHARMACOLOGY WASHINGTON UNIVERSITY ST. LOUIS, MISSOURI UNIVERSITY OF WISCONSIN MADISON, WISCONSIN	JACK L. STROMINGER M. MATSUHASHI D. N. DIETZLER ⁹
DEPARTMENT OF CHEMISTRY FACULTY OF SCIENCE NAGOYA UNIVERSITY NAGOYA, JAPAN	SAKARU SUZUKI TUNEKO OKAZAKI KAZUNORI SUGIMOTO REIJI OKAZAKI

RECEIVED MAY 19, 1964

Photochemical Isomerization of Di-*t*-butylbenzenes

Sir:

As an extension of our studies on the chemistry of *o*-di-*t*-butylbenzene,¹ we have examined the photoirradiation of this hydrocarbon. In contrast to the conversion of 1,2,4-tri-*t*-butylbenzene into a substituted bicyclo[2.2.0]hexadiene (Dewar-type "benzene") on irradiation in ether solution with a mercury arc lamp through a Vycor filter,² *o*-di-*t*-butylbenzene when similarly irradiated in an all-quartz apparatus³ undergoes a new kind of isomerization to form a 1:4 photo-stationary equilibrium mixture of *m*- and *p*-di-*t*-butylbenzene.^{4,4a}

Irradiations in our work were conducted in dilute ether solution, under nitrogen, with a 100-watt Hanovia Type 8A36 quartz-jacketed mercury light source placed

(1) A. W. Burgstahler, M. O. Abdel-Rahman, and P. L. Chien, *Tetrahedron Letters*, 61 (1964).

(2) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

(3) With the use of a Vycor filter (No. 7913), only unidentifiable products, which darkened rapidly in air, could be obtained.

(4) After communication of these results to Professor van Tamelen, we were grateful to learn that he also has obtained similar findings in the photoirradiation of *o*-di-*t*-butylbenzene.

(4a) NOTE ADDED IN PROOF.—Since submission of this paper, related photoisomerizations of other dialkylbenzenes have been reported by K. E. Wilzbach and L. Kaplan [*J. Am. Chem. Soc.*, **86**, 2307 (1964)]. Using a much higher intensity light source, these workers observed isomerizations of *o*- and *m*-xylene which we have not been able to detect under our conditions, even after prolonged irradiation.

in a water-cooled quartz immersion well. Product isomer ratios were estimated by characteristic absorption peaks in the infrared and/or n.m.r. spectra. Results of a typical run (510 mg. of *o*-di-*t*-butylbenzene in 1 l. of ether) are summarized in Table I, from which it is noted that the first stage of the isomerization was complete in about 70 hr. Likewise, starting from either *m*- or *p*-di-*t*-butylbenzene, the same photostationary composition was reached. Unfortunately, considerable amounts of unidentified by-products were also formed, and the total yield of mixed di-*t*-butylbenzenes after 75 hr. was found to be only about 20% as estimated by n.m.r. analysis.

TABLE I
PHOTOCHEMICAL ISOMERIZATION OF *o*-DI-*t*-BUTYLBENZENE IN ETHER

Time, hr.	Composition of isomeric di- <i>t</i> -butylbenzenes			Estimation method
	<i>ortho</i>	<i>meta</i>	<i>para</i>	
0	100%
6	80	20%	Traces	Infrared
18	60	30	10%	Infrared
41	15	55	30	Infrared
64	5	50	45	Infrared
76	...	50	50	Infrared
112	...	30	70	N.m.r.
146	...	20	80	N.m.r.
158	...	20	80	N.m.r.

The same type of photoisomerization also occurs with *o*-*t*-butyltoluene, but at only one-fifth the above rate. However, after 36 hr. of irradiation, no isomerization could be detected with *o*- and *m*-xylene,^{4a} *p*-*t*-butyltoluene, *o*-terphenyl, and 1,3,5-tri-*t*-butylbenzene. When a substituent such as nitro,¹ acetyl,⁵ or methoxyl⁵ was present in the 4-position of 1,2-di-*t*-butylbenzene, the isomerization was strongly inhibited.

In another experiment, irradiation of a mixture of *t*-butylbenzene and 1,3,5-*t*-butylbenzene failed to yield any detectable amount of di-*t*-butylbenzenes. Likewise, even after prolonged irradiation, none of the di-*t*-butylbenzenes showed any tendency to disproportionate into mono- and tri-*t*-butylbenzene.⁶ Consequently, these photochemical isomerizations appear to be intramolecular in nature.

When the photoirradiation of *o*-di-*t*-butylbenzene was conducted in olefin-free petroleum ether (b.p. 35–40°), the rate of formation of *m*- and *p*-di-*t*-butylbenzene was much slower than in ether, and considerable amounts of colored by-products were also produced. Other experiments with photosensitizers⁷ such as benzophenone revealed little dependency of the isomerization on the presence of such substances.

Mechanistically, these isomerizations can be accounted for either by photoinitiated 1,2-migrations of a *t*-butyl group or by excitation of the benzene ring to a Ladenburg-type structure with subsequent rearomatization to form the *meta* and thence the *para* isomer. We hope to distinguish these two possibilities by appropriate ring labeling with C¹⁴, since there is no actual carbon-carbon migration of a *t*-butyl group in the latter pathway.

(5) Preparation described in the Ph.D. thesis of P. L. C., University of Kansas, 1964.

(6) Such disproportionation is well known in Friedel-Crafts reactions of di- and tri-*t*-butylbenzenes. Cf. P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

(7) Cf. J. Saltiel and G. S. Hammond, *ibid.*, **85**, 2515 (1963).

Acknowledgment.—We are grateful to Professor Earl S. Huyser for the use of the quartz irradiation apparatus and lamp. We also thank the Alfred P. Sloan Foundation and the National Science Foundation for generous financial support of this work.

(8) Alfred P. Sloan Research Fellow, 1961–1964.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

ALBERT W. BURGSTÄHLER⁸
PING-LU CHIEN

RECEIVED MAY 26, 1964

Eight-Coordinate Complexes of Cobalt(II). A Principle Influencing the Occurrence of High Coordination Numbers¹

Sir:

Several years ago, compounds containing the tetranitratocobaltate(II) ion, $[\text{Co}(\text{NO}_3)_4]^{2-}$, were reported from several laboratories.^{2,3} On the basis of its magnetic moment and its visible and infrared spectra, this complex ion was assigned a tetrahedral structure. However, as a result of subsequent investigations^{4,5} of the compounds $\text{Co}(\text{R}_3\text{MO})_2(\text{NO}_3)_2$, $\text{R} = \text{CH}_3$ or C_6H_5 , $\text{M} = \text{P}$ or As , it was suggested that bidentate nitrate ions might also occur in $[\text{Co}(\text{NO}_3)_4]^{2-}$ with the over-all arrangement of oxygen atoms about the metal ion being such as to produce a ligand field of approximately tetrahedral symmetry, even though the actual disposition of oxygen atoms would not have this shape. We wish to report that a single crystal X-ray structure determination of $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Co}(\text{NO}_3)_4]$ demonstrates that this is indeed the case, each nitrate ion being bidentate, and the Co(II) being eight-coordinate in a dodecahedral complex.

The complex was prepared by mixing stoichiometric quantities of $\text{As}(\text{C}_6\text{H}_5)_4\text{Cl}$, AgNO_3 , and CoCl_2 in acetonitrile. After separating the insoluble AgCl by decantation, the solution was condensed to an oil by evaporation, and the remaining acetonitrile was extracted into ether. The complex was then recrystallized from a chloroform solution by addition of CCl_4 . The unit cell is monoclinic, $a = 23.47$, $b = 11.34$, $c = 18.57$ Å., $\beta = 107^\circ$, and contains two formula units. The space group is $\text{C}2/c$ and the cobalt atoms occupy special positions requiring the $[\text{Co}(\text{NO}_3)_4]^{2-}$ ions to have C_2 symmetry axes. The eight oxygen atoms surrounding the cobalt atom lie at the vertices of a distorted dodecahedron. Figure 1 shows some of the important bond distances and interbond angles at the present stage of refinement, in which only isotropic temperature factors have been used. The complete structure can be obtained by rotating each of the nitrate ions shown about the C_2 axis.

Within the limits of error, the $[\text{Co}(\text{NO}_3)_4]^{2-}$ ion has only C_{2v} , rather than D_{2d} symmetry, but it is useful to divide the eight Co–O bonds into just two sets. In one, consisting of bonds from Co to O_{I} and O_{IV} , the Co–O distances are in the normal range for Co–O bonds, 2.02 and 2.05 Å.; in the other set of bonds, from Co to O_{II} and O_{V} , they are much longer, 2.41

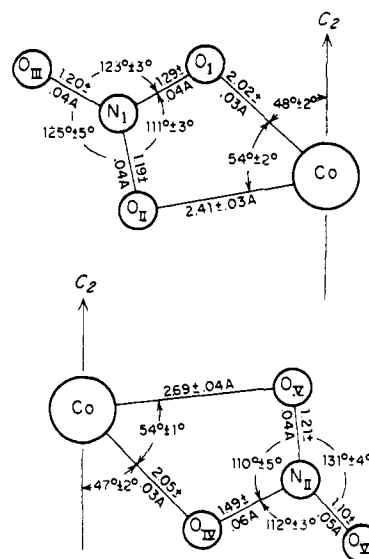


Figure 1.

and 2.69 Å., but still short enough to indicate a definite Co–O bonding interaction. The four short bonds approximately define an elongated tetrahedron with a vertical angle of $45\text{--}50^\circ$, while the four long ones define a severely flattened tetrahedron—very nearly a square—with a vertical angle of about 170° .

It has also been found that an analogous compound containing $(\text{CF}_3\text{COO})^-$ in place of $(\text{ONO}_2)^-$ can be prepared, *viz.*, $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Co}(\text{O}_2\text{CCF}_3)_4]$. This has essentially the same spectrum and magnetic moment as the nitrate complex. It crystallizes in the tetragonal system, space group $\text{I}4_1/a$, $a = 11.68$ Å., and $c = 40.82$ Å., with four formula units per cell. It is thus required that the Co atoms lie at special positions with 4 symmetry and this makes it seem likely that the $[\text{Co}(\text{O}_2\text{CCF}_3)_4]^{2-}$ ion has an eight-coordinate structure similar to, but more regular than, that of $[\text{Co}(\text{NO}_3)_4]^{2-}$, although this is not absolutely required. A thorough investigation of the structure is in progress.

We believe that from the above results and other data in the literature, an interesting and useful structural principle may be inferred, namely, that a polyatomic ligand in which two *chemically equivalent* atoms are held much closer together than such a pair of atoms would be if independent of each other has a tendency to interact through both of the equivalent atoms in such a way that the mean positions of the pairs of atoms lie roughly at the vertices of one of the usual (*e.g.*, octahedral or tetrahedral) coordination polyhedra. This is a generalization of the earlier suggestion⁵ that in the $\text{Co}(\text{R}_3\text{PO})_2(\text{NO}_3)_2$ compounds, each nitrate ion as a whole occupies a vertex of a distorted tetrahedron about the cobalt ion.

In the $[\text{Co}(\text{NO}_3)_4]^{2-}$ ion, this tendency is manifested in the fact that all four of the nitrate ions present two oxygen atoms to the cobalt ion, and the centers of the nitrate ions (the N atoms) lie at the vertices of a flattened tetrahedron, the two N–Co–N angles bisected by the molecular C_2 axis being 152 and 144° . However, if lines are drawn to points along the $\text{O} \cdots \text{O}$ lines within nitrate ions, such that these points lie at distances from each oxygen atom which are inversely proportional to the distances of the oxygen atoms from the cobalt atom, angles between these lines are very

(1) Research supported by a grant from the U. S. Army Research Office.

(2) F. A. Cotton and T. G. Dunne, *J. Am. Chem. Soc.*, **84**, 2013 (1962).

(3) D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).

(4) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

(5) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).