When the magnetic sector was set to pass only ions of m/e 15 and the accelerating voltage was scanned (electric sector voltage being kept constant at $0.5000E$), two peaks were observed (Figure 2).

Peak A corresponds to 30^{2+} ions which have lost 23 ± 2 eV of energy, while peak B corresponds to ions that have lost 29 ± 2 eV. First and second ground-state ionization potentials of NO are 9.25 and 39.8 eV.[11] The difference, 30.6 eV, is in good agreement with the position of peak B. Studies on metastable NO^+ ions[12] have revealed the existence of a highly populated excited NO^+ state 16.9 eV above the neutral molecule. The difference between the energy of this state and the second ionization potential of NO is 22.9 eV, which could very well explain the position of peak A.

It should be emphasized that what we have assayed above is the preliminary analysis of some novel experimental observations.[13] Such possibilities as energy absorption by the collision gas or formation of the doubly charged product in an excited form may, however, be necessary for a complete explanation of the observed peak shapes.

Acknowledgment. Support of the National Science Foundation (GP 16743) is acknowledged.

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(11) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, Superintendent of Documents, Washington, D. C., 1969, pp 116, 117.

(12) T. O. Tiernan and R. E. Marcotte, *J. Chem. Phys.*, **53**, 5 (1970).

(13) Seibl[14] has observed the formation of doubly charged ions from superexcited singly charged ions in the absence of a collision gas. This reaction bears some relation to those studied here but kinetic energy loss was apparently not involved.

(14) J. Seibl, *Org. Mass Spectrom.*, **2**, 1033 (1969).

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The Preparation and Structure of 2,3,7,8-Tetrachloro-*p*-dioxin and 2,7-Dichloro-*p*-dioxin

Sir:

Current interest in chlorinated dibenzo-*p*-dioxins originated because these compounds are potential impurities in chlorinated phenols and phenol esters, and because 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and hexachlorodibenzo-*p*-dioxin produce severe untoward biological effects.[1] This concern prompted us to establish methods for characterizing some of these compounds. In a conjoining effort,[2] Rowe and others have studied the toxicological properties of the chlorinated dioxins and evaluated in particular the teratogenic[3] and toxic[2,4] effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Available evidence[2] suggests that 2,7,-dichlorodibenzo-*p*-dioxin possesses a low order of toxicity. We describe below the procedures followed in preparing and isolating two chlorinated dibenzo-*p*-dioxins, and their unambigious identification by X-ray diffraction.

2,7-Dichlorodibenzo-*p*-dioxin (DCBD) was prepared by heating a mixture of potassium 2,4-dichlorophenate and a copper catalyst, prepared according to Brewster and Groening,[5] in a stirred slurry with tetralin at 185–210° for 26 hr. The solid product which separated after cooling was collected by filtration and washed with aqueous sodium hydroxide and with alcohol. A single recrystallization from anisole produced the DCBD with an assay of 99.3% as determined by mass spectroscopy.

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCBD)[6] can be prepared by treating either dibenzo-*p*-dioxin[7] or DCBD in hot chloroform solution with chlorine for periods of 16–20 hr in the presence of catalytic amounts of ferric chloride and iodine.[8] We found that this procedure gave a mixture of chlorinated dibenzo-*p*-dioxins which was predominantly the tetrasubstituted product. Separation of TCBD from the tri- and pentachloro isomers was difficult. Repeated extractions with boiling chloroform, alternated with recrystallizations from anisole, gave after fractional sublimation TCBD which assayed 98% by mass spectroscopy and 98.5% by vapor phase chromatography. The observed melting point was 305° and the heat of fusion was measured to be 9300 cal/mol. Differential scanning calorimetry showed a single exotherm.

The two crystal structures were determined by very similar techniques, and their essential parameters as obtained in our experiments are summarized in Table I. A Picker four-circle automatic diffractometer was used to determine the lattice constants and to gather intensity data in the θ–2θ scan mode using monochromatic Mo Kα radiation. The structures were solved from the Patterson function and refined by full-matrix least-squares assuming anisotropic temperature factors for Cl, O, and C and isotropic temperature factors for H. The assignment of the centric space group $P1$ was initially based on intensity statistics and subsequently supported by the anomalous behavior of the metric and thermal parameters upon refinement in $P1$. Corrections were applied for absorption and for anomalous scattering by Cl, and, in the case of TCBD, a secondary extinction correction was also made.

The TCBD crystal contains two independent molecules, A and B, situated on the inversion centers at (0, 0, 0) and (1/2, 1/2, 1/2), respectively; in DCBD the unique molecule lies on the center at (0, 0, 0). All three molecules approach planarity very closely: no non-hydrogen atom is more than 0.02 Å from the least-

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(1) (a) *Chem. Eng. News*, **48**, 60 (April 27, 1970); (b) E. Hegyi, Z. St'ota, and A. Luptakova, *Berufsdermatosen*, **6**, 327 (1969); (c) G. R. Higginbotham, A. Huang, D. Firestone, J. Verett, J. Ress, and A. D. Campbell, *Nature*, 220, 702 (1968); (d) E. L. Jones and H. Krizek, *J. Invest. Dermatol.*, **39**, 511 (1962); (e) K. H. Schulz, *Arbeitsmedizin-Socialmedizin-Arbeitshygiene*, **3**, 25 (1968).

(2) V. K. Rowe, J. M. Norris, B. A. Schwetz, G. L. Sparschu, P. J. Gehring, J. L. Emerson, and C. G. Gerbig, presented at the 160th National Meeting of the American Chemical Society, Washington, D. C., Sept 17, 1971.

(3) G. L. Sparschu, F. L. Dunn, and V. K. Rowe, *Food Cosmet. Toxicol.*, in press.

(4) W. N. Piper and J. P. Rose, presented at the 160th National Meeting of the American Chemical Society, Washington, D. C., Sept 17, 1971.

(5) R. Q. Brewster and T. Groening, "Organic Synthesis," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 445.

(6) *Warning:* 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is extremely toxic. Techniques used in handling radioactive and infectious materials are applicable to TCBD and include the use of lab coats, throw-away plastic gloves, safety glasses, a laboratory hood adequate for radioactive work, isolated work areas properly identified, minimization of contaminated waste, and safe waste handling and disposal. Hands and forearms should be thoroughly washed after each manipulation.

(7) M. Tomita, S. Ueda, and M. Narisada, *Yakugaku Zasshi*, **79**, 186 (1959).

(8) W. Sandermann, H. Stockman, and R. Casten, *Chem. Ber.*, **90**, 690 (1957).

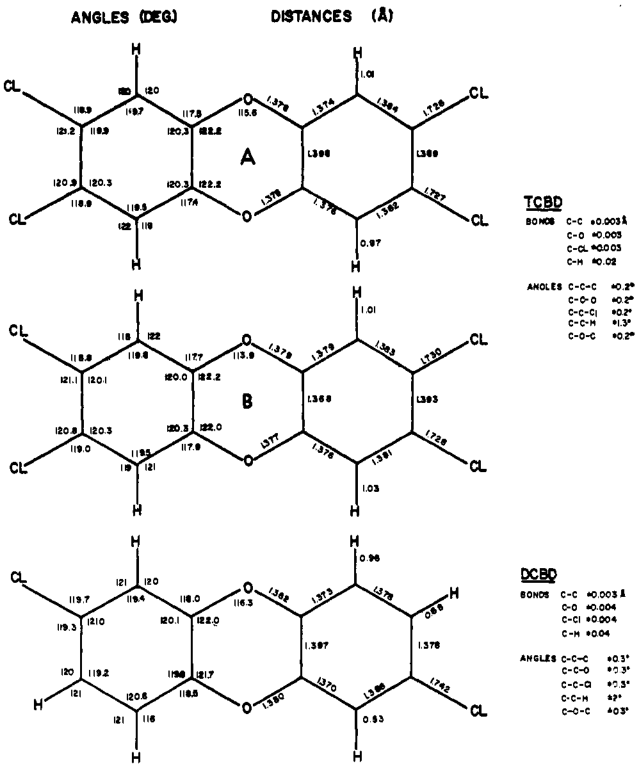
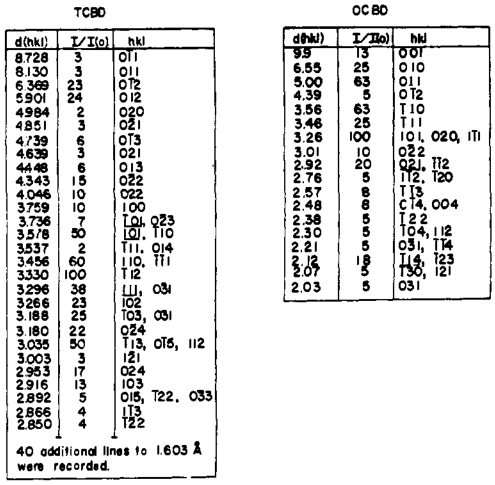


Figure 1. Bond distances and angles and their standard deviations in TCBD and DCBD. All molecules possess a crystallographic center of symmetry.

squares molecular plane. In both crystals, the molecules form stacks along the short x axes. Because the normals to the molecular planes are tilted with respect to the translation direction (by 24.4° for TCBD–A, 22.6° for TCBD–B, and 25.9° for DCBD), the distances between the molecular planes (3.446 Å for TCBD–A, 3.493 Å for TCBD–B, and 3.489 Å for DCBD) are somewhat shorter than the corresponding lattice periods. Bond distances and angles, and their standard deviations, are given in Figure 1; their values show excellent internal consistency and also agree well with accepted literature values.[9] Further details of these structures will be published elsewhere.[10] The reader is also referred to the crystal structure of 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin which has been reported by Cantrell, Webb, and Mabis.[11]

Table I. Crystal Data

	TCBD	DCBD
Molecular formula	$C_{12}H_4O_2Cl_4$	$C_{12}H_6O_2Cl_2$
Molecular weight	321.977	253.086
Crystal habit	Lath	Lath
Long direction	a	a
Major faces	$\{01\bar{1}\}$	$\{010\}$
Crystal size, mm	1.30 × 0.396 × 0.072	1.50 × 0.022 × 0.096
Space group	$P\bar{1}$	$P\bar{1}$
Cell constants (25°)		
a, Å	3.783 ± 0.003	3.878 ± 0.003
b, Å	9.975 ± 0.009	6.755 ± 0.009
c, Å	15.639 ± 0.015	10.265 ± 0.015
α, deg	94.14 ± 0.02	99.46 ± 0.01
β, deg	95.20 ± 0.04	100.63 ± 0.03
γ, deg	92.77 ± 0.04	99.73 ± 0.03
Unit cell volume, Å^3	585.3 ± 0.4	255.2 ± 0.1
Density (calcd), g cm^{-3}	1.827 (Z = 2)	1.647 (Z = 1)
Linear absorption coeff (Mo Kα), cm^{-1}	9.79	5.26
No. of reflections measured	2666	1152
No. of reflections above background	2381	1030
$R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.036	0.057
$R_2 = \{\Sigma\, w(F_o - F_c)^2/\Sigma w F_o{}^2\}^{1/2}$	0.038	0.062



TCBD

d(hkl)	I/I(o)	hkl
8.728	3	$0\bar{1}1$
8.130	3	011
6.369	23	$0\bar{1}2$
5.901	24	012
4.984	2	020
4.851	3	$0\bar{2}1$
4.739	6	$0\bar{1}3$
4.639	3	021
4.448	6	013
4.343	15	$0\bar{2}2$
4.046	10	022
3.759	10	100
3.736	7	$\underline{\bar{1}01}$, $0\bar{2}3$
3.578	50	$\underline{101}$, $\bar{1}10$
3.537	2	$\bar{1}11$, 014
3.456	60	110, $\bar{1}\bar{1}1$
3.330	100	$\bar{1}12$
3.296	38	$\underline{111}$, 031
3.266	23	102
3.188	25	$\bar{1}03$, 031
3.180	22	$0\bar{2}4$
3.035	50	$\bar{1}13$, $0\bar{1}5$, 112
3.003	3	$1\bar{2}1$
2.953	17	024
2.916	13	103
2.892	5	015, $\bar{1}22$, 033
2.866	4	$1\bar{1}3$
2.850	4	$\bar{1}22$
40 additional lines to 1.603 Å were recorded.		

DCBD

d(hkl)	I/I(o)	hkl
9.9	13	001
6.55	25	010
5.00	63	011
4.39	5	$0\bar{1}2$
3.56	63	$\bar{1}10$
3.46	25	$\bar{1}11$
3.26	100	101, 020, $1\bar{1}1$
3.01	10	$0\bar{2}2$
2.92	20	021, $\bar{1}\bar{1}2$
2.76	5	$1\bar{1}2$, $\bar{1}20$
2.57	8	$\bar{1}\bar{1}3$
2.48	8	$0\bar{1}4$, 004
2.38	5	$\bar{1}22$
2.30	5	$\bar{1}04$, 112
2.21	5	$0\bar{3}1$, $\bar{1}\bar{1}4$
2.12	18	$\bar{1}14$, $\bar{1}23$
2.07	5	$\bar{1}30$, 121
2.03	5	031

Figure 2. X-Ray powder diffraction data for TCBD and DCBD (courtesy of H. W. Rinn). The data for TCBD were obtained on a 115-mm diameter AEG (Allgemeine Elektrizitäts-Gesellschaft) Guinier camera using Seeman-Bohlin focusing and Cu Kα_1 radiation (λ 1.5405 Å). The DCBD data were taken with a 143.2-mm diameter Debye–Scherer camera using Cu Kα radiation (λ 1.5418 Å).

We have found X-ray powder diffraction to be very expeditious in identifying laboratory samples of chlorinated dioxins, and accordingly we give the observed powder patterns of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,7-dichlorodibenzo-p-dioxin in Figure 2.

Acknowledgment. We thank P. P. North, T. P. Blumer, M. A. Neuman, and J. J. Flynn for assistance with various phases of this study.

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(9) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 18 (1965).

(10) We have also recently completed the crystal structures of 2,8-dichlorodibenzo-p-dioxin (space group $Pnam$, a = 5.983 (6), b = 7.114 (10), c = 24.637 (36) Å, Z = 4) and octachlorodibenzo-p-dioxin (space group $P2_1/c$, a = 12.009 (9), b = 3.828 (3), c = 16.297 (9) Å, β = 101.14 (3)°, Z = 2).

(11) J. S. Cantrell, N. C. Webb, and A. J. Mabis, *Acta Crystallogr., Sect. B*, 25, 150 (1969).

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Reactions of Coordinated Nucleophiles. Formation and Structure of a Novel Tridentate Complex

Sir:

This publication reports a novel rapid reaction involving condensation of coordinated ligands to give a tridentate amidine. *cis*-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ reacts in near neutral or basic solution to give a purple complex with the constitution $[Co(en)(NH_2CH_2C(NH_2){=}NCH_2CH_2NH_2)Cl]^{2+}$ (abbreviated I-Cl, ϵ_{max} 214 M^{-1} cm^{-1} at 552 nm, 25°, 1 M NaClO$_4$) where one end of a bidentate ethylenediamine ligand has con-