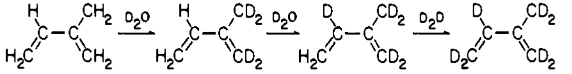
exchange. For example, in the isoprene anion the four allylic hydrogens exchange most rapidly ($k = 9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). A fifth proton, which we formulate as that in the 3 position, exchanges more slowly but at a rate which is similar enough to that of the first four to prevent a reliable dissection of its intrinsic exchange rate constant. The final two hydrogens exchange more slowly still with an estimated rate constant of 1×10^{-11} cm^3 molecule^{-1} s^{-1} (eq 7).[10] Thus, by determining not only the



(7)

maximum number of exchangeable hydrogens but also their relative ease of exchange, we can gain important information about the structure of the carbanion. Further, in bracketing hydrocarbon acidities the presence or absence of multiple exchanges may serve to fix an upper or lower limit for certain types of hydrogens in the molecule. For instance, we have found that in the 2-*tert*-butylallyl anion only the four allylic hydrogens exchange with D_2O.

We are presently examining the potential of other compounds for use as exchange agents in different hydrocarbon acidity ranges. The details of our efforts in this area shall appear in a forthcoming publication.

Acknowledgment. We are grateful to the National Science Foundation for financial support under Grant CHE79-09750.

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(10) We do not mean to imply by eq 7 that complete exchange of one type of hydrogen occurs before the other exchange begins but rather that differences in exchange rates can be seen in the mass spectrum.

Dication Ethers (R^+-O-R^+), Conjugated Cations with Remarkably Low Rotation Barriers. A Theoretical Investigation

Yitzhak Apeloig* and Dorit Arad

Department of Chemistry
Technion—Israel Institute of Technology
Haifa 32000, Israel

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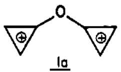
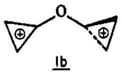
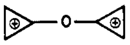
Stang and co-workers[1] recently reported the preparation of novel dication ether salts, R^+-O-$R^+ \cdot 2CF_3SO_3^-$, where R was cyclopropenylium, tropenylium, pyridinium, etc. These novel carbenium ions raise a number of intriguing questions regarding their structures, preferred conformations, rotation barriers, stabilities, and charge distributions. Experimental difficulties have so far frustrated the attempts to answer these questions.[1] This information can be obtained computationally by the application of reliable molecular orbital methods.[2,3] Thus we were prompted to study these species theoretically with both semiempirical and ab initio methods, and in this communication we report the results of these calculations for two dications, dicyclopropenylium ether (**1**) and ditropenylium ether (**2**), both synthesized by Stang.[1]

The dications **1** and **2** were calculated in both planar (**1a**, **1c**, **2a**) and perpendicular (**1b**, **1d**, **2b**) conformations. For **1**, calculations were carried out with both the semiempirical MINDO/3 method[4] and standard ab initio methods.[5] For the larger **2** only


1a


1b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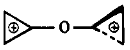
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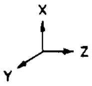

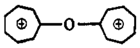
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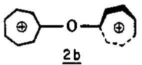
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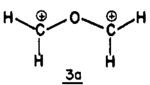
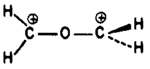
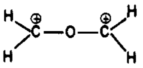
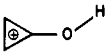
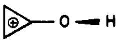
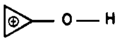

3a


3b


3c


4a


4b


4c

MINDO/3 was used. Each structure was fully optimized by using MINDO/3 (for **1** and **2**) and the minimal STO-3G[6a] basis set (for **1**).[7] For **1**, single point calculations with the extended 4-31G basis set[6b] at the optimized STO-3G geometries followed. For comparison, we have carried out similar calculations for the parent ether dication $^+CH_2OCH_2^+$ (**3**) and the hydroxycyclopropenium cation (**4**). The total and relative energies of **1**–**4** are given in Table I.

What is the preferred conformation of these dications? The hydroxycyclopropenium cation is more stable in the bent planar conformation **4a**, where the empty cationic 2p(C^+) orbital is conjugated with the $2p_y$ lone pair of oxygen. In the perpendicular conformation **4b**, the 2p(C^+) orbital is conjugated with the sp^2 lone pair of oxygen. Due to its lower energy[8] an sp^2 orbital is less effective than a 2p orbital in stabilizing an adjacent empty orbital.[9] Consequently, **4b** is less stable than **4a** by 11.3 kcal mol^{-1} (4-31G, Table I). In the dications the situation is more complex. In the bent planar conformations (e.g., **1a**) only *one* lone pair [i.e., $2p_y$(O)] is conjugated with the two electron deficient rings. In the bent perpendicular conformations (e.g., **1b**) on the other hand, each ring is conjugated with a different lone pair of oxygen so that two lone pairs participate in conjugation. Linear perpendicular conformations (e.g., **1d**) which have a pseudoallenic structure are especially attractive in this respect. Linearization at oxygen is, however, unfavorable energetically,[10] because the sp^2(O) lone pair is transformed to a 2p(O) lone pair of higher energy.[8] Is the stabilization resulting from such double conjugation large enough to favor the perpendicular structures (e.g., **1b** or **1d**) over the planar structures (e.g., **1a**)? Qualitative arguments do not lead to a secure prediction.

The calculations point to a delicate balance between the various effects, resulting in a relatively small energy difference between the planar and the perpendicular conformations. The dicyclopropenylium ether dication is most stable in the *bent planar conformation* **1a** (arc ∠COC = 119.6°, STO-3G) but the rotation barrier around the COC bonds are remarkably small (Table I). The **1a**–**1b** energy difference is 5.85 kcal mol^{-1} (4-31G, 5.55 kcal mol^{-1} at STO-3G), much smaller than the corresponding rotation barriers in **4** (11.3 kcal mol^{-1}, 4-31G),[11a] $HOCH_2^+$ (22.5 kcal

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(1) Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361. Stang, P. J.; Maas, G.; Smith, D. L.; McCloskey, J. A. *Ibid.*, in press.

(2) For recent reviews of MO calculations of carbenium ions, see: (a) Hehre, W. J. In "Applications of Electronic Structure Theory"; Schaefer, H. F., III. Ed.; Plenum Press: New York, **1977**; Vol. 4, pp 277–331. (b) Radom, L.; Poppinger, D.; Haddon, R. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, **1976**; Vol. 5, pp 2303–2426.

(3) For recent calculations of dications, see: (a) Clark, T.; Weiss, R. *J. Org. Chem.* **1980**, *45*, 1790. (b) Radom, L.; Schaefer, H. F., III. *J. Am. Chem. Soc.*, **1977**, *99*, 7522. (c) Craig, D. P.; Radom, L.; Schaefer, H. F., III *Aust. J. Chem.* **1978**, *31*, 261. (d) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302.

(4) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302.

(5) The Gaussian 70 series of programs were used: Hehre, W. J.; Latham, W. A.; Ditchfield, R.; Newton, M.; Pople, J. A. Program No. 236, QCPE, Indiana University, Bloomington, IN.

(6) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Hehre, W. J., Pople, J. A. *Ibid* **1972**, *56*, 4233.

(7) The optimized structures of **1**–**4** are provided as supplementary material to this paper.

(8) In H_2O, for example, the energy difference between these orbitals is 2.1 eV. See: Turner, D. W. "Molecular Photoelectron Spectroscopy"; Wiley: London, 1970.

(9) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976.

(10) Linear H_2O, for example, is by 35.6 kcal mol^{-1} (6-31G*) less stable than H_2O in its optimal geometry.

(11) (a) These rotation barriers are not sensitive to the basis set used; e.g., at 6-31G* the rotation barriers in **4** is 12.2 kcal mol^{-1}. (b) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. *Can. J. Chem.* **1975**, *53*, 1144. (c) Fărcasiu, D.; Horsley, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4906.

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Table I. Calculated Total Energies (Hartree), Heats of Formation (kcal mol^{-1}), and Relative Energies (kcal mol^{-1})

	total energies		relative energies			
cation	STO-3G[a]	4-31G[b]	MINDO/3[a]	STO-3G	4-31G	MINDO/3
1a	−299.80481	−303.04934	491.5	0.0	0.0	0.0
1b	−299.79596	−303.04001	492.0	5.5	5.8	0.5
1c	−299.76118	−303.03765	494.2	27.4	7.3	2.7
1d	−299.76592	−303.04158	492.0	24.4	4.9	0.5
2a			394.5			3.3
2b			391.2			0.0
3a	−150.12539	−151.76460	519.1	0.0	12.8	13.1
3b[c]	−150.12377	−151.78508	506.0	1.0	0.0	0.0
3c	−150.08484	−151.75395	519.4	25.5	19.5	13.4
4a	−187.48367	−189.56463	170.3	0.0	0.0	0.0
4b	−187.46338	−189.54654	177.0	12.7	11.3	6.7
4c	−187.42286	−189.54285	185.0	38.2	14.7	14.7

[a] Using fully optimized structures. Provided as supplementary material. [b] At the optimized STO-3G geometries. [c] The bent perpendicular conformation collapses upon optimization to the linear 3b.

mol^{-1}, 4-31G),[11b] and $H_3COCH_2^+$ (20.8 kcal mol^{-1}, 4-31G).[11c] The linear pseudoallenic conformation **1d** is by 4.9 kcal mol^{-1} (4-31G) less stable than **1a**. At 4-31G linear **1d** is actually more stable than the bent **1b** by 0.9 kcal mol^{-1}. However, on the basis of 6-31G* calculations of model compounds we estimate that in the gas phase the relative energies of **1a–d** are (kcal mol^{-1}) **1a**, 0.0, **1b**, 5–6; **1c**, 12–15; **1d**, 10–12.[11a,12] The increased stabilization which results from the substitution of the $sp^2(O)-2p(C^+)$ conjugation in **1b** by the more efficient $2p(O)-2p(C^+)$ conjugation in **1d**, compensates for the unfavorable linearization at oxygen.[10] As expected the "doubly conjugated" **1d** is more stable than **1c**, but the rotation barrier is only 2.4 kcal mol^{-1} (4-31G).[11a] The low rotation barriers in **1** (i.e., **1a** $\rightleftarrows$ **1b** and **1c** $\rightleftarrows$ **1d**) which are most unusual in light of the strong oxygen–cyclopropenium conjugation (see below) and the partial double-bond character of the C–O bonds[13a] are associated with the ability of oxygen to adjust its electron donation to the electron demand of the adjacent cationic centers.[13b] In **1b** for example, 0.146 electrons are transferred from the $2p_y(O)$ orbital to the planar cyclopropenium ring (i.e., the ring in the *XZ* plane). In **1a**, charge transfer from the $2p_y(O)$ orbital increases substantially to 0.250 electrons so that each of the cyclopropenium rings receives 0.125 electrons—nearly the same as in **1b**.[13a] Our results imply that at room temperature **1** is *freely rotating and inverting* around the central COC bonds.[12] The inversion process, however, may be "frozen out" at lower temperatures. This conclusion is consistent with the ^{13}C NMR spectra of the tetra-*n*-propyl derivative of **1**, which shows only two signals for the cyclopropenium ring carbons. Three and five signals are expected for **1a** and **1b**, respectively. The linear structures **1c** and **1d** which in principle are also consistent with the NMR data[1] are less stable than **1a** (Table I).[12]

The ditropenylium ether dication is more stable according to MINDO/3 in the *linear perpendicular* conformation **2b** (Table I). The linear conformation **2a** is favored over the bent conformation even when the two rings occupy the same plane. This unusual linearization at oxygen is due, in addition to the conjugation effect discussed above, primarily to steric interactions between the ortho hydrogens of the tropylium rings, especially in the planar conformation.[14] In ditropylium carbenium ions such as $NCC^+(C_7H_6)_2$ where considerable widening of the $C_7H_6^+$ angle is impossible, these interactions are relieved by rotation of the rings out of a common plane.[15] In **2**, bent partially rotated propeller type structures are less stable than **2b**. Although MINDO/3 underestimates the inversion barriers at oxygen (by ca. 0–6 kcal mol^{-1} relative to the 4-31G values and ca. 12 kcal mol^{-1} relative to the 6-31G* values[12]), our experience with **1** shows that the conclusion that **2** is linear will probably hold at higher values of theory. Even if **2b** is slightly bent it should have a very low barrier to inversion.[12] The calculated barrier for rotation around the C–O bond in **2** is 3.3 kcal mol^{-1}. As MINDO/3 underestimates such barriers by ~5 kcal mol^{-1} (Table I), we conclude that the rotation barrier in **2** is ~8–9 kcal mol^{-1}, and hence, the ditropenylium ether dication **2** is freely rotating around the C–O bond at room temperature, in agreement with the ^{13}C NMR data.[1]

The stabilities of the ether dications **1–3** are compared with those of the corresponding hydroxymonocations in the hydrolysis eq 1–3, respectively.[16]

$$\mathbf{1a} + H_2O \rightarrow 2\cdot(\mathbf{4a}) \qquad (1)$$

$$\mathbf{2b} + H_2O \rightarrow 2\cdot(c\text{-}C_7H_6OH^+) \qquad (2)$$

$$\mathbf{3b} + H_2O \rightarrow 2\cdot(HOCH_2^+) \qquad (3)$$

As expected these hydrolysis reactions are highly exothermic, reflecting the relief of the strong electrostatic repulsions between the positive charges in the dications. The heats of hydrolysis decrease in the order **3** > **1** > **2**, i.e., $\Delta E(\mathbf{3})$ = 164.0 kcal mol^{-1} (4-31G), 139.1 kcal mol^{-1} (MINDO/3); $\Delta E(\mathbf{1})$ = 110.9 kcal mol^{-1} (4-31G), 97.4 kcal mol^{-1} (MINDO/3); $\Delta E(\mathbf{2})$ = 69.9 kcal mol^{-1} (MINDO/3). The heats of hydrolysis decrease and the stabilities of the dications increase when the two charges are located farther away from each other. The strongest electrostatic repulsions exist in **3**, where the positive charges can be transferred from the adjacent carbons only to the methylene hydrogens. The electrostatic repulsions are smaller in **1** and reduced farther in **2**, where the charge is delocalized over the entire molecular framework. The high heats of hydrolysis do not necessarily imply that the ether dications should dissociate spontaneously. Several fragmentation routes of **1** were investigated and found to be endothermic, suggesting that if these dications are generated with little excess energy they might be observed in the gas phase.[17] Ether dications

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(12) Preliminary 6-31G* calculations indicate that the true inversion barriers at oxygen are probably intermediate between the STO-3G and the 4-31G values. Compare, for example, the following inversion barriers (kcal mol^{-1}): in **4**, 38.2 (STO-3G), 13.7 (4-31G), 23.6 (6-31G*), 14.7 (MINDO/3); in $HOCH_2^+$, 29.6 (STO-3G), 12.0 (4-31G); 22.0 (6-31G*) 8.3 (MINDO/3); in $H_3COCH_2^+$, 24.9 (STO-3G), 11.6 (4-31G), 18.2 (6-31G*), 2.8 (MINDO/3); in H_2O, 71.2 (STO-3G), 26.3 (4-31G), 35.6 (6-31G*) 29.3 (MINDO/3). Note, however, that in $H_3COCH_2^+$ the *measured* inversion barrier in super acid media[11b] of 11.9 kcal mol^{-1} is closer to the 4-31G than to the 6-31G* value. Apparently, solvation reduces these inversion barriers. **1** may behave similarly.

(13) (a) Using the Mulliken population analysis: Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833. Full details will be reported elsewhere; (b) A referee has pointed out that this phenomena is more generally referred to as "equalization of electronegativity". See: Ray, N. K.; Samuels, L.; Parr, R. G. *J. Chem. Phys.* **1979**, *70*, 3680.

(14) In a bent planar conformation with arc ∠COC = 150°, the distance between two ortho hydrogens is 0.53 Å. The H–H distance is short, 2.52 Å, also in the linear **2a**. Even in bent perpendicular structures steric interactions are appreciable. Thus, with arc ∠COC = 150°, the ortho hydrogen of one ring is 2.42 Å from the plane of the adjacent perpendicular tropylium ring.

(15) Sundaralingham, M.; Chwang, A. K. *Carbonium Ions* **1976**, *5*, 2427–2476.

(16) Equations 1–3 are not isodesmic and may include a relatively large error (see: Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A., *J. Am. Chem. Soc.* **1970**, *92*, 4796). However, the energies calculated in isodesmic comparisons of the ether dications with the monohydroxycations such as the hydride transfer equation, $\mathbf{1a} + 2(c\text{-}C_3H_3OH) \rightarrow 2\cdot(\mathbf{4a}) + (c\text{-}C_3H_3)_2O$, are similar to those of eq 1–3. We therefore prefer to use eq 1–3, where all structures are fully optimized as a convenient guide to stability.

similar to **1** were indeed detected by field desorption mass spectrometry.[1] In the solid state or solution, the repulsive electrostatic interactions should be reduced by interactions with anions (i.e., $CF_3SO_3^-$) or the solvent, increasing the stability of dications toward dissociation and allowing their isolation as relatively stable species.[1] Preliminary calculations indeed show that the hydrolysis of the neutral salt (c-C_3H_2)$_2O^{2+}\cdot 2Cl^-$ is much less exothermic than the hydrolysis of the dication.

In conclusion, the ether dications which were recently synthesized[1] are predicted to be essentially freely rotating and inverting around the central C–O–C bonds at room temperature. The preferred conformers range from bent planar (in **1**) to linear perpendicular in **2** and **3**.[18] Further studies on these and related[1] novel species (e.g., the cyclopropyldicarbinyl dication[19]) are under way and will be reported in a full paper.

Acknowledgment. We thank Professor P. J. Stang for bringing this problem to our attention, making his data available to us prior to publication, and valuable discussions. This research was partially supported by a grant from the United States—Israel Binational Science Foundation (BSF), Jerusalem, Israel.

Supplementary Material Available: Optimized structures of **1–4** (MINDO/3) and **1**, **3**, and **4** (STO-3G) in the form of Z matrixes (8 pages). Ordering information is given on any current masthead page.

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(17) For example, the fragmentation of **1a** to c-$C_3H_2O^{+\cdot}$ + c-$C_3H_2^{+\cdot}$ is endothermic by 14.1 kcal mol^{-1} (MINDO/3).

(18) We emphasize that our calculations apply to the isolated dications in the gas phase. Extrapolation of our conclusions to solution or the solid state, where interactions with the solvent and the anions are very important, should be done cautiously.

(19) Lammertsma, K.; Cerfontain, H. *J. Am. Chem. Soc.* **1980**, *102*, 3257, 4258.

(20) **Note Added in Proof**: The inclusion of correlation energy by using the perturbation procedure suggested by Møller and Plesset (see: J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem.*, **S10**, 1 (1976)) has little effect on the calculated barriers to inversion at oxygen. Thus, compare the following inversion barriers (kcal mol^{-1}) at MP2/6-31G* and at RHF/6-31G* (in parentheses): H_2O 36.7 (35.6), $HOCH_2^+$ 24.2 (22.0), for **3a** → **3c** 22.4 (18.3). These results reinforce our conclusions in ref 12. We thank Dr. T. Clark (Erlangen) for running these MP2/6-31G* calculations.

Gas Chromatographic Separation and Identification of the Four Stereoisomers of 1,2,2-Trimethylpropyl Methylphosphonofluoridate (Soman). Stereospecificity of in Vitro "Detoxification" Reactions

Hendrik P. Benschop,* Cornelis A. G. Konings, and Leo P. A. de Jong

Prins Maurits Laboratory TNO
2280 AA Rijswijk, The Netherlands

Received December 19, 1980

The nerve agent 1,2,2-trimethylpropyl methylphosphonofluoridate, $Me_3CCHMeO(Me)P(O)F$ (soman), is notorious for its extreme toxicity[1] and refractoriness with regard to the standard medical treatment for anticholinesterase intoxication.[2,3] Toxicological studies of this agent are complicated by the presence of two chiral centers in the molecule, leading to four stereoisomers.[4] These isomers may vary widely in their (i) rate of inhibition of cholinesterases[7] and overall toxicity,[8] (ii) response to reactivators of the inhibited enzyme,[9] (iii) rate of aging of the inhibited enzyme,[7] and (iv) rate of "detoxification" in the body.[10,11] We now report a rapid and convenient GLC -method for the separation of the four stereoisomers of soman. These isomers have been identified and the usefulness of the method for toxicological studies is demonstrated.

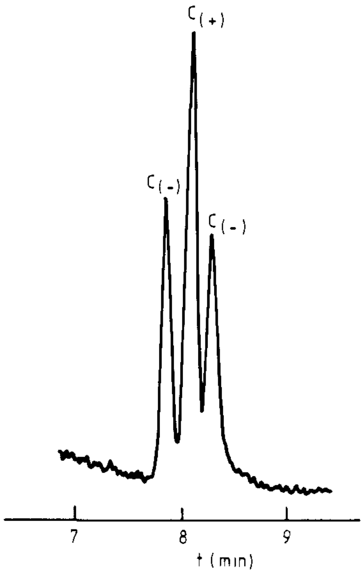

Figure 1. Gas chromatogram of soman after injection of a 1-μL sample of a 4-mM solution of soman in i-PrOH on a Chirasil-Val column (l = 25 m, ϕ = 0.3 mm; plate number 3 × 10^4, peak 1), column temperature 80 °C, precolumn pressure 103 kPa, injection split ratio 1:10. The injection block and the FID-detector block of the Pye-104 gas chromatograph were held at 300 °C.

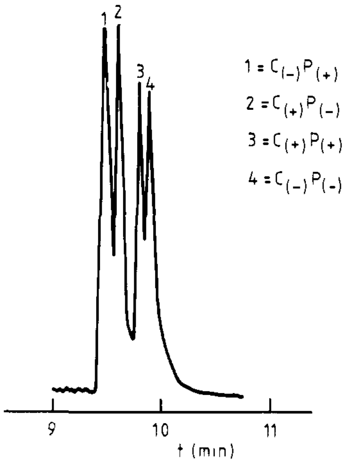

Figure 2. Gas chromatogram of soman on a Carbowax 20M/Chirasil-Val column. The Carbowax 20M column (l = 30 m, ϕ = 0.3 mm) was coupled directly to the same Chirasil-Val column as described in Figure 1. The Carbowax leg of the system was connected with the injection port of the gas chromatograph. The theoretical number of plates of the combined column is 1.3 × 10^5 (peak 1). See Figure 1 for further chromatographic conditions.

In order to separate enantiometric compounds by means of GLC, an optically active stationary phase should be used.[12] We

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(1) Warning: In view of its extreme toxicity, soman and other nerve agents should be handled only in specialized laboratories, where trained medical personnel is continuously present.

(2) "Medical Protection against Chemical-Warfare Agents"; SIPRI Books; Almquist & Wiksell: Stockholm, 1976.

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