



Designing low-ionization potential analogs of tetrakis-dimethylamino-ethylene (TMAE) using density functional calculations

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ABSTRACT

A number of analogs of the photosensitive molecule TMAE (tetrakis-dimethylamino-ethylene) have been investigated computationally with the goal of lowering the vertical ionization potential (IP_v). This is of importance in UV-photodetectors based on gas photoionization and multiplication. The low IP_v of TMAE, 6.11 eV, is shown to be due to resonance stabilization of the cation. N-substitution of phenyl groups and p-substitution of tertiary amines on the latter are found to be efficient ways of lowering IP_v . The compound trans-bis-(p-dimethylaminophenyl, methyl)aminoethylene is calculated to have a IP_v considerably lower than TMAE (about 5.5 to 5.7 eV) and appears to be a promising synthetic target.

INTRODUCTION

The detection and imaging of photons in many fields of applied science has become a very demanding task, due to the increasing complexity of modern scientific instrumentation. In such areas of application as particle physics and medical imaging, one is often required to cover a very large area with a gigantic number of photon detectors, capable of providing fast, time-resolved images of a single or a few photons at very high repetition rates. Besides direct recording of images, an important application is photon recording from scintillating fibers and crystals excited by x-ray or gamma radiation. This is the case in computer tomography (CT) scanners, gamma cameras, and positron emission tomography (PET).

Vacuum photomultiplier tubes are expensive devices, and are limited in size and in localization resolution. The detection of photons with detectors based on photoelectron multiplication in photosensitive gases is a very interesting alternative [1,2], which has already been well proven and developed in many laboratories for imaging of single UV photons. Such devices, having sensitive areas of several square meters, are currently employed in particle physics experiments [3]. The most attractive photosensitive vapors are tetrakis(dimethylamino)ethylene (TMAE) [4] and triethylamine (TEA) [1]. TMAE has a very broad spectrum of sensitivity, a cutoff at 230 nm, and a very large quantum efficiency (QE) [5]. It is therefore used in most of the particle physics experiments employing UV-photon imaging detectors and also in photon imaging detectors for PET, i.e. localizing gamma-induced photons from BaF₂ crystals [6].

A serious drawback of TMAE is its reactivity with oxygen and with many detector construction materials. The tendency, therefore, has been to replace TMAE by other photosensitive materials, both gases and solids. It was found that solid CsI UV-photocathodes could substitute for TMAE vapors [7], albeit with a non-negligible loss of efficiency. In this case photoelectrons emitted from the CsI surface are multiplied in a gaseous electron multiplier. However, the quantum efficiency of CsI to the scintillation light from most useful scintillators, such as BaF₂ and in particular its fast components at 195 and 220 nm [8], is very limited due to the cutoff at 220nm. Several other photosensitive organic compounds were studied[9], in particular metallocenes. The best material in this group is ethylferrocene[10], but its QE is much inferior to that of TMAE in magnitude and in cutoff.

It is therefore clear that the development and synthesis of new photosensitive materials with improved chemical stability and reduced photoionization threshold would broaden the useful range of applications of gaseous photon imaging detectors.

Recent advances in computational chemistry, in particular in the area of density functional theory [11,12], have made possible the computation of a variety of molecular properties to a chemical useful accuracy for medium-sized molecules. This opens the perspective of computer aided design of new photosensitive materials.

In the present article we will present such a study in which we consider various analogs of TMAE. Firstly, we will demonstrate that we can actually compute the property of interest to the required accuracy. Secondly, we will explore the reason for TMAEs unique properties in this context. Thirdly, we propose a new possible detector compound with a predicted vertical ionization potential that is about 0.4 eV below that of TMAE, and potentially a greatly improved quantum efficiency in the range around 200 nm.

COMPUTATIONAL METHODS

The calculations were carried out using the SPARTAN¹ graphical front-end and molecular mechanics modules running on the DEC Alpha 500/500 in the Computational Chemistry Group and GAUSSIAN 94 revision D.4² running on the former machine and the DEC TurboLaser 2100 at the Weizmann Institute Computer Center (WICC).

Starting geometries were generated using the SYBYL molecular mechanics force field [13] as implemented in SPARTAN. Choices between different conformers of the same molecule were made on the basis of the lowest SYBYL strain energy or, when the differences there were smaller than 0.1 kcal/mol, on the basis of calculations for the different conformers using the PM3 semiempirical method of Stewart [14], as implemented in SPARTAN.

Full geometry optimizations were subsequently carried out using density functional theory with the Becke 3-parameter-Lee-Yang-Parr (B3LYP) exchange-correlation functional [15,16]. The suitability of this hybrid method for computing a wide variety of properties is well established now[17,18]: very recently, its success for ionization potentials was also demonstrated [19].

¹SPARTAN version 4.1.2, Wavefunction, Inc., 18401 Von Karman Avenue, Irvine, CA 92715, USA, ©1995 Wavefunction, Inc.

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Because of the large size of most of the molecules under study, we limit ourselves to two basis sets. The first is Dunning's correlation consistent polarized valence double-zeta basis set (cc-pVDZ) [20], which appeared to produce ionization potential essentially as good as those obtained with much larger basis set in Ref.[18]. It is of [3s2p1d/2s1p] contracted size (14 basis functions per first-row, 5 per hydrogen atom). The second is the standard 4-21G basis set [21], which is only of [3s2p/2s] quality but requires only 9 basis functions per first-row atoms and two per hydrogen atom. It was previously shown that B3LYP calculations with 4-21G and cc-pVDZ basis sets yield very similar results for such diverse properties as the potential energy surfaces of protonated clusters [22] and harmonic vibrational spectra of polyacenes (e.g. compare [23] with [24,25]). If we can show that the ionization potentials obtained with this basis set are still of acceptable quality, then fairly large molecules can be treated.

RESULTS AND DISCUSSION

All computed vertical and adiabatic ionization potentials (IP_v and IP_a , respectively) are given in Table 1, together with any available experimental values.

Concerning the general quality of the results, two observations can immediately be made. The first is that the quality of the B3LYP/cc-pVDZ results seems surprisingly good. For example, the computed IP_a values for ethylene (10.27 eV), TEA (7.18 eV), and TMAE (4.95 eV) are in very good agreement with the respective experimental values of 10.507 ± 0.004 eV [26], 7.11–7.5 eV [26], and $\leq 5.36(2)$ eV [27,28]. On average, they appear to be systematically on the low side by about 0.2–0.3 eV. Since basis set extension will normally favor the neutral species more than the cation (since the latter has, after all, one electron less), basis set incompleteness is normally expected to lead to underestimated IPs.

The second observation, likewise, is that B3LYP/4-21G appears to systematically produce substantially lower IPs than B3LYP/cc-pVDZ. The differences appear to be the smallest for planar, semirigid structures (e.g. phenylaminoethylene), and larger for nonplanar, nonrigid ones (e.g. TEA). For instance, for triethylamine we calculate $IP_v = 6.93$ eV at the B3LYP/4-21G level and 7.89 eV at the B3LYP/cc-pVDZ level, compared to 6.97 and 7.08 eV, respectively, for phenylaminoethylene (vinylaniline). In the former case, the differences are substantially smaller for IP_a . Since polarization functions will have an appreciable effect in nonplanar cases

on bond and torsion angles, while these are more or less constrained in planar cases, the different behavior can be rationalized.

It was previously noted [19] that expanding the basis set from cc-pVDZ to aug-cc-pVDZ [29] (i.e. including one low-exponent "anion" function of each angular momentum) increases B3LYP computed IP_a values for {N,O,F} containing compounds by amounts ranging from 0.3 eV for NH_3 over 0.5 eV for H_2O to 0.6 eV for HF. In the present work, we find for amino-ethylene that the corresponding basis set augmentation increases the computed IP_v and IP_a values both by 0.22 eV, compared to only 0.08 eV for C_2H_4 . Unfortunately, B3LYP/aug-cc-pVDZ calculations with full geometry optimization are simply not computationally feasible for most of the species considered in this work.

Let us now investigate the substituent effects on ethylene for the B3LYP/cc-pVDZ "model chemistry".

Adding a single amino group to ethylene lowers its IP_v by about 2.6 eV. Adding a second amino group geminally (in "as-" position) only seems to further reduce IP_v by 0.1 eV (the effect goes up to 0.4 eV at the B3LYP/4-21G level), compared to about 0.7 eV for cis- or trans-substitution (1.1 eV at the B3LYP/cc-pVDZ level). On IP_a , however, we see the following lowerings at the B3LYP/cc-pVDZ level: as -0.77, cis -1.33, trans -1.54 eV. This clearly suggests the importance of resonance for stabilizing the cation (i.e. lowering the IP): while the two nitrogen atoms and the central C=C bond are part of a single resonant system in the cis and trans cases, they are divided over two resonant systems in the "as-" case. This is further underscored by the fact that tri-aminoethylene actually has a *higher* vertical ionization potential than either cis- or trans- di-methylaminoethylenes.

We also note that trans-diamination yields an IP_a about 0.2 eV lower than cis-diamination, although the IP_v values are nearly identical.

In the case of tetra-amino-ethylene, however, the third and fourth amino groups, together, lower the ionization potential further (compared to cis-or trans-diamino-ethylene) by some 0.8 eV (or, at the B3LYP/4-21G level, 0.9 eV). In this molecule, of course, there is a wide variety of resonance structures that can be drawn for the cation, and that lead to its stabilization. This was previously suggested [28] to be the reason for the low IP_v of TMAE.

The effect of the amino groups on the IP_v now being understood, the next question is: what is the effect of secundarization and tertiarization of the amino groups, and of the specific substituents being used? Apparently, replacing all the hydrogens in TAE (tetra-aminoethylene) with methyl groups (to produce TMAE) will lower the IP by some 0.8 eV at the B3LYP/cc-pVDZ level.

We have investigated this in detail by considering a number of N-substituted mono-aminoethylenes. Adding a single methyl group is calculated to lower the IP_v by 0.09 eV at the B3LYP/cc-pVDZ level, albeit of 0.34 eV at the B3LYP/4-21G level. (For IP_a , lowerings of about 0.4 eV are found with both basis sets.) Adding a second methyl lowers IP_v by a further 0.28 eV at the B3LYP/cc-pVDZ level (0.19 eV at the B3LYP/4-21G level). The use of a single tertiary butyl group instead of two methyl groups delivers essentially the same effect on IP_v , but a slightly larger one on IP_a .

If this effect were linked to the electron-donating character of the methyl groups, then using a strongly electron-withdrawing substituent would surely increase the IP_v . And indeed, this is what we observe: turning amino-ethylene into trifluoroacetamido-ethylene actually *increases* IP_v by 1.3 eV, at both the B3LYP/4-21G and B3LYP/cc-pVDZ levels. (The increases in IP_a are 1.2 and 1.1 eV, respectively.) Again, the explanation appears to be obvious, namely that electron donating groups on atoms involved in the resonant system that includes the HOMO will further enhance stabilization of the cation, and therefore lower the ionization energy.

Extending the resonant system *itself*, however, appears to be rather more profitable than substituting electron-donating groups *on* the resonant system. That is, substituting a single phenyl group on amino-ethylene is calculated to cause a lowering in IP_v of about 0.8 eV (and in IP_a of about 0.7 eV) at both the B3LYP/4-21G and B3LYP/cc-pVDZ levels. Note that at both levels, the structure of the neutral molecule is found to be planar (i.e., with sp^2 hybridization at N), contrary to the alkyl-N-substituted aminoethylenes which are nonplanar and exhibit bond angles around N that suggest sp^3 hybridization. (Interestingly, the computed geometry for TAE exhibits an almost perfectly sp^2 hybridized N atom — which probably explains the relatively low IP in that case.)

However tetrakis-(phenylamino)ethylene, not to mention tetrakis-(diphenylamino)-ethylene, would be so sterically hindered as to not only be exceedingly difficult synthetic targets, but also probably to present a deviation from planarity

so large as to seriously impair resonance stabilization of the cation, and therefore lowering of the IP.

A series of calculations on substituted di(phenylamino)ethylenes at the B3LYP/cc-pVDZ level would become rather too time-consuming. Since, however, all qualitative trends appear to be well reproduced at the B3LYP/4-21G level, we will use this level of theory from now on, and will reserve B3LYP/cc-pVDZ for our final compound of choice.

We have considered cis- and trans-diphenylaminoethylenes. These are calculated to have IP_v values of 6.12 and 5.95 eV, respectively, clearly moving in the right direction. (Both for IP_v and for IP_a , trans substitution appears to yield lower values than cis substitution.)

The obvious next candidate would be the use of various substituents on the phenyl group. Initial experimentation at the PM3 level showed that sensitivity was largest at the para site, as well as that the effect on the IP_v was strongly correlated to the Hammett constant of the substituent, with (as expected) electron-donating groups yielding a decrease in IP_v . At the B3LYP/4-21G level, we see, for example, that para-substitution of chlorine increases IP_v by 0.2 eV, but that substituting an amino group instead decreases it by 0.9 eV.

Since the most electron-donating neutral substituent on the Hammett scale is dimethylamino-, the compound bis-(p-dimethylamino-phenyl)aminoethylene would be a prime candidate for a compound with a lower IP_v than TMAE.

We then see that the trans isomer of this compound is predicted to have a IP_v of 4.88 eV, which is indeed appreciably lower than the calculated value of 5.28 eV for TMAE at that level (B3LYP/4-21G). The difference in IP_a , however, is essentially zero. Note that although the molecule is not planar and has only C_i symmetry, the deviation from planar C_{2h} symmetry is rather small. For the cis isomer, however, the strain between the phenyl groups causes a large deviation from planarity, leading to a (fairly small) increase in IP_v to 4.97 eV. (The of 0.18 eV in IP_a is somewhat larger.) Since the cis-isomer is calculated to be about 3 kcal/mol more stable than the trans isomer, this will probably be the prevailing form resulting from synthesis.

What effect would tertiarizing the central amines have? First of all, strain in the cis isomer would be such that essentially only the trans isomer would have to be

considered. Secondly, the amines would be better protected against oxidation. Thirdly, IP_v would be even lower, if anything. Upon tertiarization of the amine in trans-bis(phenyl,methyl)amino-ethylene we see a drop of the B3LYP/4-21G IP_v from 5.95 to 5.72 eV. It is therefore not surprising that trans-bis-(p-dimethylaminophenyl,methyl)aminoethylene is found to have the lowest B3LYP/4-21G IP_v of all the compounds considered in the present work: 4.82 eV, the corresponding IP_a being 4.65 eV. Repeating our calculation with the cc-pVDZ basis set, we find $IP_v=5.23$ eV — about 0.4 eV lower than TMAE — and $IP_a=4.92$ eV, comparable to TMAE. (It is worth noting that this calculation, including full geometry optimizations of the neutral and the cationic species starting from an initial HF/4-21G geometry for the neutral, took about two weeks of CPU time on the DEC Alpha 500/500.)

Given on the one hand the apparent tendency of B3LYP/cc-pVDZ to underestimate IP_v values by 0.2 to 0.3 eV, and on the other hand assuming that the difference between computed and observed IP_v will be similar as for TMAE, we can probably expect the measured IP_v to lie in the 5.5—5.7 eV (218—225 nm) range, and the IP_a in the 5.2—5.4 eV (230—238 nm) range.

While the computed IP_a suggests a cutoff similar to TMAE, the lowering of the computed IP_v by 0.4 eV (which corresponds to an increase of about 15 nm in that range) suggests that the quantum efficiency for ionization of this compound should rise much more steeply as the wavelength is decreased from the cutoff than for TMAE (see e.g. Ref. [26], p. 13, for an explanation). In particular for detection of the fast components of a BaF₂ scintillator (195 and 220 nm) this could potentially mean a very substantial improvement in performance.

The compound has C_i symmetry but is calculated to be fairly close to planarity. In order to facilitate its identification after synthesis, its computed (B3LYP/4-21G) harmonic frequencies have been given in Table 2, together with double-harmonic IR intensities for the a_u modes. For comparison with experiment, scaling of CH stretching harmonic frequencies by 0.96, and of other frequencies by 0.975, is recommended [25,30]. As expected, a molecule of this size has quite a few infrared features: the most prominent ones outside the CH stretching region are calculated at 849, 934, a pair at 1318 and 1340, and 1566 cm^{-1} . Given the absence of polarization functions in the basis set, some reservations are due concerning the quality of the computed infrared intensities, which should be kept in mind while comparing to the observed spectrum.

CONCLUSIONS

In this study, we have been able to establish the following:

- the very low vertical ionization potential (IP_v) of TMAE is due to resonance stabilization of the cation;
- the best way to reduce the IP_v appears to be extension of the aromatic system by N-substitution of phenyl groups, followed by adding electron-donating N-substituents. Electron-withdrawing ones increase it;
- further reductions can be achieved by p-substitution of tertiary amines on the phenyl groups;
- the compound trans-bis-(p-dimethylaminophenyl,methyl)aminoethylene is calculated to have a IP_v substantially below that of TMAE (and therefore potentially a markedly increased quantum efficiency in the range important for BaF₂ based scintillation counters), and is suggested as a synthetic target for the generation of new compounds with low photoionization thresholds which may improve the characteristics of UV-photon detectors.

ACKNOWLEDGMENTS

JMLM is an Honorary Research Associate ("Onderzoeksleider in eremandaat") of the National Science Foundation (Belgium) and a Yigal Allon Fellow. AW holds the Rebecca and Israel Sieff Chair in Organic Chemistry. AB holds the W. P. Reuther Chair in the Peaceful Use of Atomic Energy. This work was partially supported by the Foundation Mordoh Mijan de Salonique and by the Israel Science Foundation. The authors thank Dr. J. Va'vra (Stanford Linear Accelerator Center), Dr. P. Miné (Ecole Polytechnique, Palaiseau, France) and Mr. Facundo Fernandez for stimulating discussions and Mr. Pablo Amster for technical assistance with some of the calculations.

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TABLE 1. computed vertical (IP_v) and adiabatic (IP_a) ionization potentials, and observed values (eV)

	Point group	Computed (B3LYP/)				Observed IP_a
		4-21G	4-21G	cc-pVDZ	cc-pVDZ	
		IP_v	IP_a	IP_v	IP_a	
C_2H_4	D_{2h}	10.53	10.30	10.48 ^a	10.27 ^a	10.507(4) ^b
triethylamine	C_3	6.93	6.77	7.89	7.18	7.50 ^c
tetrakis-(dimethylamino)ethylene	D_2	5.28	4.65	5.62	4.95	$\leq 5.36(2)$ ^d
aminoethylene	C_s	7.72	7.55	7.89 ^e	7.72 ^e	[8.20] ^b
as diaminoethylene	C_2	7.28	6.57	7.75	6.95	
cis diaminoethylene	$=C_2$	6.61	5.93	7.15	6.39	
trans diaminoethylene	C_2	6.61	5.73	7.19	6.18	
triaminoethylene	C_1	6.87	5.46	7.33	5.96	
tetraaminoethylene	D_2	5.74	4.69	6.42	5.32	
methyl-aminoethylene	C_1	7.38	7.15	7.80	7.35	
dimethyl-aminoethylene	C_1	7.19	6.94	7.52	7.16	
tbutyl-aminoethylene	C_1	7.15	6.85	7.56	7.08	
acetamido-ethylene	C_s	8.37	8.06	8.55	8.24	
trifluoroacetamidoethylene	C_s	9.06	8.75	9.15	8.83	
phenyl-aminoethylene	C_s	6.97	6.91	7.08	7.02	
p-chlorophenylaminoethylene	C_s	7.17	7.10			
p-aminophenylaminoethylene	C_1	6.09	5.93			
cis-di(phenylamino)ethylene	C_2	6.12	5.94	—	—	
trans-di(phenylamino)ethylene	C_i	5.95	5.72	—	—	
trans-di(methyl,phenylamino)ethylene	C_i	5.72	5.50			
trans-bis-(p-aminophenyl)aminoethylene	C_i	4.94	4.74			
trans-bis-(p-dimethylaminophenyl,methyl)aminoethylene	C_i	4.82	4.65	5.23	4.92	
cis-bis-(p-dimethylaminophenyl)aminoethylene	C_1	4.97	4.86			
trans-bis-(p-dimethylaminophenyl)aminoethylene	C_i	4.88	4.68			

(a) B3LYP/aug-cc-pVDZ values: $IP_v=10.54$, $IP_a=10.34$ eV

(b) Lias et al. [26]

(c) recommended value of Lias et al. [26], but values of 7.11 eV and 7.20 eV are also given there

(d) Nakato et al. [28]; $IP_v=6.11$ eV in that ref.

(e) B3LYP/aug-cc-pVDZ values: $IP_v=8.11$, $IP_a=7.94$ eV

TABLE 2. Computed (B3LYP/4-21G) vibrational frequencies (cm^{-1}) for trans-bis-(p-dimethylaminophenyl,methyl)aminoethylene. Infrared intensities in km/mol for the a_u bands are given in parentheses

A_g	40.8, 53.8, 58.4, 78.3, 83.0, 143.0, 176.9, 197.0, 217.8, 247.5, 258.9, 291.6, 313.9, 405.8, 414.1, 443.1, 466.5, 508.8, 554.5, 595.2, 675.4, 745.5, 759.1, 816.7, 823.8, 844.7, 849.4, 954.2, 963.2, 973.1, 986.2, 1038.3, 1083.3, 1149.5, 1152.5, 1166.4, 1166.6, 1174.8, 1213.0, 1260.1, 1262.2, 1276.2, 1333.7, 1342.8, 1374.0, 1375.5, 1401.2, 1477.3, 1489.4, 1495.5, 1526.4, 1539.5, 1542.7, 1548.9, 1568.1, 1577.3, 1585.1, 1588.1, 1596.1, 1654.8, 1700.4, 2975.7, 2990.1, 2998.8, 3025.5, 3028.4, 3050.5, 3125.9, 3138.6, 3160.2, 3198.6, 3202.4, 3208.5, 3227.8, 3230.7
A_u	10.7(0.5), 27.9(1.6), 31.5(1.3), 61.2(13.0), 78.4(0.4), 86.0(13.9), 120.1(4.9), 177.0(1.0), 200.1(2.6), 211.5(5.3), 218.5(1.4), 294.7(2.8), 312.9(2.7), 346.1(12.3), 436.0(3.3), 441.9(7.2), 451.0(7.5), 482.8(11.5), 514.3(7.6), 551.1(26.8), 586.4(27.1), 671.0(2.3), 675.8(1.1), 759.3(8.0), 792.8(2.2), 821.9(1.0), 849.0(166.2), 934.1(231.6), 954.7(72.8), 963.8(5.8), 979.4(11.6), 1013.1(238.5), 1038.6(2.4), 1083.3(77.9), 1140.3(410.7), 1149.5(0.1), 1158.8(18.5), 1166.4(0.2), 1172.2(17.5), 1211.0(74.1), 1238.7(70.8), 1265.9(54.2), 1273.5(91.9), 1318.2(473.4), 1339.5(537.2), 1371.6(415.4), 1399.4(27.1), 1423.4(127.6), 1476.3(14.8), 1489.4(1.4), 1496.3(19.9), 1525.8(109.4), 1539.5(1.0), 1542.3(13.9), 1548.9(20.5), 1566.1(760.5), 1577.2(11.6), 1584.8(86.5), 1586.3(147.4), 1596.0(123.3), 1654.0(15.9), 2975.0(130.2), 2990.1(197.7), 2998.6(152.2), 3025.5(0.3), 3028.4(201.3), 3050.8(75.9), 3125.9(3.9), 3138.5(102.0), 3160.1(31.6), 3198.6(34.7), 3204.3(22.8), 3214.8(41.0), 3227.9(39.5), 3230.6(18.2)

