$u(t)$	continuous fluorescence response function
$f(t)$	real continuous time profile of the exciting flash
$e(t)$	continuous response function of the electronics
$z(t)$	real fluorescence continuous time profile of the system excited by a Dirac pulse
$g(t)$	continuous flash response function
$z_1(t)$, $z_2(t)$	single exponential components in a biexponential decay
$u_1(t)$, $u_2(t)$	components of $u(t)$ in the biexponential decay case
$u'(t)$	continuous fluorescence response function with a scattered light component
$su(t)$	integral of $u(t)$ on $(0, t)$
$sg(t)$	integral of $g(t)$ on $(0, t)$
$ssu(t)$	integral of $su(t)$ on $(0, t)$
$ssg(t)$	integral of $sg(t)$ on $(0, t)$
$U(i)$	number of counts in the ith channel of the fluorescence histogram
$G(i)$	number of counts in the ith channel of the flash histogram
$SU(i)$	sum of $U(j)$'s on $(0, i)$
$SG(i)$	sum of $G(j)$'s on $(0, i)$
$SU'(i)$	approximate sum of $U(j)$'s on $(0, i - {}^1/_2)$
$SG'(i)$	approximate sum of $G(j)$'s on $(0, i - {}^1/_2)$
$\overline{U(i)}$	quantized convolution product of $g(t)$ with $z(t)$, the parameters having been determined by the phase plane method

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Structural Information from Tandem Mass Spectrometry for China White and Related Fentanyl Derivatives

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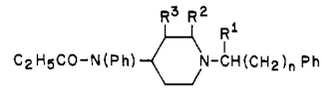
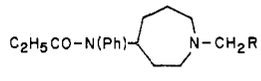
The potential of tandem mass spectrometry utilizing collisionally activated dissociation (CAD) for molecular structure determination is illustrated with α-methylfentanyl ("China White"), whose complex structure required several methods for its original elucidation. CAD spectra of fragment ions in its electron ionization (EI) mass spectrum provide information on dissociation pathways and fragment structures; the latter information comes from both interpretation and matching against reference spectra. Although the EI spectrum shows no odd-electron and few primary fragment ions, ion types most useful for such CAD studies, CAD data from the even-electron, secondary fragment ions gave sufficient structural information.



1: $R^1 = CH_3$, $R^2 = R^3 = H$, $n = 1$
2: $R^1 = R^3 = H$, $R^2 = CH_3$, $n = 1$
3: $R^1 = R^2 = H$, $R^3 = CH_3$, $n = 1$
4: $R^1 = R^2 = R^3 = H$, $n = 1$
5: $R^1 = R^2 = R^3 = H$, $n = 0$



6: R = cyclopropyl
7: R = Ph
8: R = CH_2Ph
9: $PhNHCH(CH_3)$-$CH{=}CH^2$
10: $PhNHCH_2CH{=}CHCH_3$
11: $PhN(CH_3)CH_2$-$CH{=}CH_2$
12: $PhCH_2N[CH(CH_3)$-$CH{=}CH_2]_2$

Elucidation of the molecular structure of China White, an illicit narcotic implicated in drug overdose deaths, attracted unusually wide publicity (*1–3*). Structure 1 was assigned on the basis of mass, infrared, and nuclear magnetic resonance spectra; synthesis corroborated this identification, eliminating 3 as a candidate. The unusual narcotic activity of this compound meant that available samples contained very small concentrations, so that it would have been especially advantageous if the complete identification could have been done with a method requiring only a submicrogram sample, such as mass spectrometry. However, spectral interpretation was difficult for this polyfunctional compound; the electron ionization (EI) mass spectrum (Figure 1) "was totally unfamiliar" (*1*). From this spectrum the Self-Training Interpretive and Retrieval System (STIRS) (*4, 5*) correctly identified the β-phenylethylamine moiety and the cyclic amine but gave little indication of the *N*-phenylpropionamide portion of the molecule. It thus appeared that these compounds might provide an interesting test of the additional structural information available from tandem mass spectrometry (MS/MS) (*6–10*).

In MS/MS the first mass spectrometer (MS-I) is operated as a conventional instrument, forming ions from the sample by methods such as electron and chemical ionization (EI and CI). Ions of a specific mass separated by MS-I are then fragmented further, usually by metastable ion (MI) or colli-

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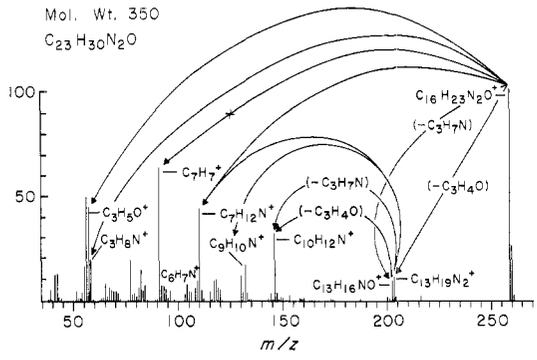


Figure 1. The electron-ionization mass spectrum of China White, compound **1**.

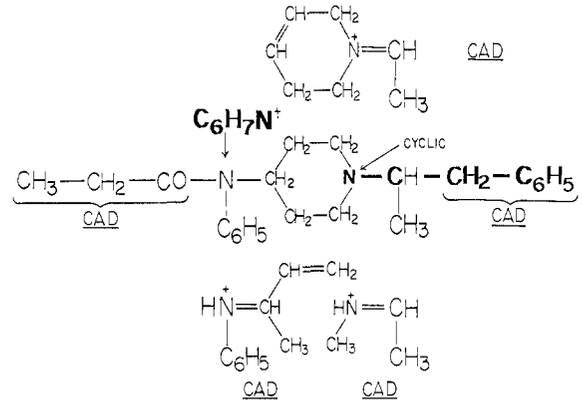


Figure 2. Structural information on China White from the normal EI mass spectrum (MS-I) in bold, plus additional information from CAD (MS-II).

sionally activated dissociation (CAD), with separation of the resulting product ions in MS-II. This secondary mass spectrum is indicative of the structure of its precursor fragment ion; the same general fragmentation rules of EI or CI mass spectra pertain. The CAD mass spectrum produced by multikilovolt ion collisions is particularly valuable. The relative abundances of these fragment ions, excluding those formed by the lowest energy reactions (peaks observed in the MI spectrum), are independent of the precursor ion internal energy and thus are quantitatively characteristic of the ion's structure (*6–10*). In normal EI and CI mass spectra the peak masses provide valuable information as to the mass of the molecule and some of its fragments; by exact measurement of these masses the corresponding elemental compositions can be determined. Early studies of CAD mass spectra (*8*) pointed out the potential utility for molecular structure determination of the additional information concerning the structures of these fragment ions available from CAD mass spectra, but little has been done to apply this technique to larger molecules for which much more information is required for structural definition. A separate study (*11*) describes the applicability of MS/MS to structure determination of oxygenated steroids, for which the CAD spectra of odd-electron fragment ions were found to be the most useful. However, the important peaks of Figure 1 represent even-electron (EE) ions; another objective of this study was to assess the value of CAD spectra of EE fragment ions for substructural assignment.

EXPERIMENTAL SECTION

CAD and MI mass spectra were measured on an MS/MS instrument utilizing a double-focusing Hitachi RMH-2 as MS-I, a He molecular beam to produce CAD, and an electrostatic analyzer as MS-II (*12*), using an ion source temperature of 130 °C, ion accelerating potential of 9.8 kV, and a collision gas pressure giving a precursor transmittance of 25%. Each CAD spectrum is a computer average of at least 20 scans. Peaks are often poorly resolved, so that the accuracy of abundance measurements of neighboring peaks is sometimes compromised. EI mass spectra (Figure 1 and Table II) were measured on a Finnigan quadrupole GC/MS instrument.

Compound **9** was synthesized from 3-chloro-1-butene and aniline with purification by silica column chromatography and **12**, from 3-chloro-1-butene and benzylamine with purification by distillation. $PhNHCH(CH_3)CH_2OH$ (**14**) was synthesized from propylene oxide and aniline under acidic condition and isolated by distillation. $PhNHCH_2CH(OH)CH_3$ (**15**) was synthesized from lithioanilide and propylene oxide and purified by column chromatography. Proton NMR and EI-MS indicated the compounds to be pure. Compounds **6–8** were supplied by Thomas N. Riley (*13*). Other compounds were purchased from Aldrich Chemical Co.

RESULTS

The CI mass spectrum and exact mass measurements of China White (**1**) indicate the molecular ion composition $C_{23}H_{30}N_2O$, m/z 350 (*1*). This corresponds to a "rings-plus-double-bonds" value of 10 (*14*); fragment ion elemental compositions (Figure 1) indicate that major parts of this involve a hydrocarbon ($C_7H_7^+$) and a one-nitrogen ($C_6H_7N^+$) fragment. STIRS indicates molecular weight 350 (*4*) and the substructures (*5*) methyl (99% reliability), benzyl (96%), $C_6H_5CH_2CN$ (12/15 best matching compounds, match factor 11.2), and saturated N-containing three- to six-membered ring (9/15, MF 11.0 and 11.1). This information is shown in bold face in Figure 2.

The small size (~700 spectra) of the current reference file of CAD mass spectra (*15*) was a serious disadvantage for this study, and so the following CAD reference spectra were catalogued. The sources of major fragment ions indicated by CAD are shown by the arrows of Figure 1.

***m/z* 57, $C_3H_5O^+$.** CAD spectra of six isomers have been measured (*16*); these are easily distinguishable, as each gives a separate base peak. For example, that from the propionyl ion corresponds to the loss of CO to form $C_2H_5^+$. The CAD spectrum of the propionyl ion is identical with those of the $C_3H_5O^+$ ions obtained from **1–4**.

***m/z* 58, $C_3H_8N^+$.** Five of these isomeric ions can be distinguished by using their CAD mass spectra (*17*). The spectrum of $C_3H_8N^+$ from **1** corresponds to the reference ion $CH_3N^+H{=}CHCH_3$.

***m/z* 91, $C_7H_7^+$.** CAD spectra of six isomeric $C_7H_7^+$ ions have been described (*18*, *19*). The CAD spectrum of $C_7H_7^+$ ions from **1** matches that for the benzyl reference ion.

***m/z* 132, $C_9H_{10}N^+$.** CAD spectra of $C_9H_{10}N^+$ ions from **9**, $PhNHCH_2CH{=}CH_2$ (**13**), **14**, and **15** were measured as references. Spectra from **1–3** were the same and matched the spectrum of these ions from **9** and **13**.

***m/z* 146, $C_{10}H_{12}N^+$.** CAD spectra of these ions from **1–3** and **5–12** are shown in Table I.

***m/z* 202, $C_{13}H_{16}NO^+$.** After separation of a small amount of $C_{14}H_{20}N^+$ by high-resolution MS, the CAD spectrum of these ions from **1** has prominent peaks at m/z 146*, 109, 77, 118, 187*, 130–131, and 91 (in order of decreasing abundance; peaks with asterisk in MI spectrum).

***m/z* 203, $C_{13}H_{19}N_2^+$.** The CAD mass spectrum of these ions from **1** has prominent peaks at m/z 146*, 111, 119, 132, 201, 93, and 57–58.

***m/z* 259, $C_{16}H_{23}N_2O^+$.** The CAD spectrum of these ions from **1** has prominent peaks at m/z 202–203*, 110–111, 57–59, 146, 154, 132, 118–120, 216, 77, 81–86, 92–97, 68–71, 159, 160, 105, 30, and 43.

DISCUSSION

For information on the whole molecule it is advantageous to examine complementary pairs of ions, whose sum of masses

Table I. CAD Mass Spectra of $C_{10}H_{12}N$ Ions, m/z 146

compd	ion structure	m/z values of fragment ion												
		51	63-6[a]	77	91	92	94	103	104	105	115	117	130-1[a]	144
1	a	54	28	100	44	13	20	52	37	30	(23)[b]	(50)	(115)	(230)
2	b	36	18	100	34	25	15	29	55	28	(13)	(35)	(135)	(230)
3[c]	c	54	19	100	54	8	5	65	54	24	(41)	(61)	(195)	(171)
5	e, a	58	42	100	(850)	(26)	<0.2	36	48	(52)	36	125	(80)	(200)
6	?	44	17	100	33	6	23	38	74	29	21	42	60	(71)
7	b, e	22	10	100	85	20	10	15	55	27	20	44	(39)	(100)
8	?	17	9	100	17	17	7	33	(66)	(44)	17	37	(43)	(90)
9[c]	a	56	23	100	49	13	13	51	37	28	(44)	(94)	(240)	(125)
10[c]	b	31	22	100	31	23	10	25	46	20	(32)	(84)	(320)	(190)
11[c]	d	34	36	100	25	20	<0.1	49	17	76[d]	(14)	(9)	(190)	(150)
12[c]	e	31	40	49	(440)	(185)	<0.1	10	34	12	37	35	32	100

[a] Incompletely resolved peaks; values are average abundances for the indicated mass range. [b] Peaks in parentheses also formed by metastable ion decomposition. [c] Used as a reference spectrum of the ion structure indicated. [d] Additional peaks at m/z 106-107 (40%).

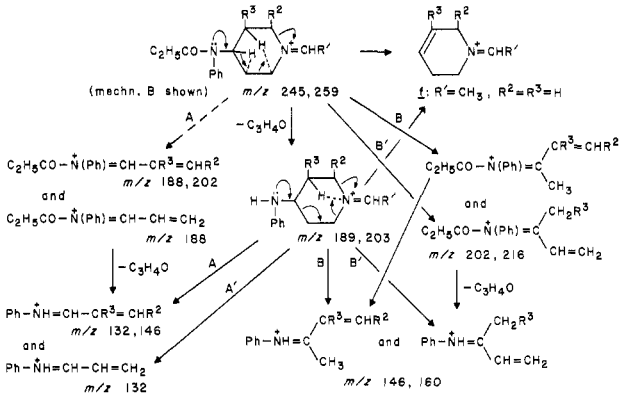
or elemental compositions equals that of the molecule (*20*). Fortunately, two significant primary ions, $C_7H_7^+$ (m/z 91) and $C_{16}H_{23}N_2O^+$ (m/z 259), comprise such a complementary pair; the CAD spectrum of the latter does not indicate that it is a precursor to the former. (The only two other peaks of significance which could be higher-mass members of a complementary pair are $C_{13}H_{19}N_2$ and $C_{13}H_{16}NO$; there are no pairing ions for these.) For the $C_7H_7^+$ ion, the CAD spectrum provides persuasive evidence for the benzyl substructure. Although $C_7H_7^+$ ions can undergo facile rearrangement, this usually produces a significant proportion of the more stable tropylium ion. In the variety of benzylic molecules studied, a high benzyl/tropylium ratio was only observed for compounds such as $PhCH_2I$ in which the benzylic bond is relatively weak (*18, 19, 21*).

The complementary $C_{16}H_{23}N_2O^+$ fragment has so many possible isomers that choosing the correct reference ion without other information was unlikely, and a further subdivision into complementary pair(s) of ions was sought. However, because $C_{16}H_{23}N_2O^+$ is an even-electron (EE) ion, a complementary pair must consist of an EE ion plus an odd-electron ion. For example, complementary ions for the EE $C_{13}H_{16}NO^+$ and $C_{13}H_{19}N_2^+$ ions (m/z 202 and 203) would be the OE ions $C_3H_7N^{+\cdot}$ and $C_3H_4O^{+\cdot}$, respectively; these are not observed, as expected from the "even-electron" rule (*22*). However, the EI mass spectrum has prominent EE ions $C_3H_8N^+$ and $C_3H_5O^+$ which could represent the same substructures; a common decomposition of EE^+ ions involves loss of a stable molecule through rearrangement of a hydrogen from that portion of the ion to the product EE^+ ion (*22, 23*). The CAD spectra of these ions define their substructures as $CH_3NH^+{=}CHCH_3$ and $C_2H_5CO^+$ and suggest that the molecules $CH_3N{=}CHCH_3$ and $CH_3CH{=}C{=}O$ were lost from exterior skeletal portions of the $C_{16}H_{23}N_2O$ fragment to form the m/z 202 and 203 ions. Because $C_2H_5CO^+$ ions are not abundant products of hydrogen rearrangements (*23*), it is likely that this substructure is also on the exterior of the molecule.

Supporting these assignments are the CAD spectra of the $C_{13}H_{16}NO^+$ and $C_{13}H_{19}N_2^+$ ions, whose numbers of possible isomers are still large for direct CAD structural identification. For both of their CAD spectra the largest peak is $C_{10}H_{12}N^+$ (m/z 146), again due to the losses of C_3H_4O and C_3H_7N. Thus the $C_{10}H_{12}N^+$ ion should represent the last unidentified piece of **1**. Structural information can be deduced from its CAD spectrum. The base peak at m/z 77 and the aromatic ion series are strong evidence for the presence of a phenyl ring. Also $-CH_2-$ is probably not adjacent to the phenyl ring, as this should cause [m/z 91] > [m/z 77].

Appropriate reference CAD spectra (Table I) were measured

Scheme I



of isomeric $C_{10}H_{12}N^+$ ions which should have the structures $PhN^+H{=}C(CH_3)CH{=}CH_2$ (a), $PhN^+H{=}CHCH{=}CHCH_3$ (b), $PhN^+H{=}CHC(CH_3){=}CH_2$ (c), $PhN^+(CH_3){=}CHCH{=}CH_2$ (d) [could also contain $PhN^+(=CH_2)CH_2CH{=}CH_2$], and $PhCH_2N^+H{=}CHCH{=}CH_2$ (e), based on their formation from **9, 10, 3** (vide infra), **11**, and **12**, respectively. These spectra make it possible to identify the $C_{10}H_{12}N^+$ ions from **1** as (a) (Figure 2). The combination of (a) with $CH_3N{=}CHCH_3$ should indicate the structure of the $C_{13}H_{19}N_2$ piece of the molecule. In addition to the phenyl ring, and the presumed double bond to the quaternary nitrogen atom, this piece must contain one ring or double bond; STIRS indicates the former. Possible structures for $C_{13}H_{19}N_2^+$ were tested by seeing which is the most rational for the formation of (a) and $CH_3N^+H{=}CHCH_3$; the best candidate and postulated mechanisms are shown in Scheme I, which is discussed below. A key indicator that the methyl group of (a) arises from a ring CH_2 group in the $C_{13}H_{19}N_2^+$ ions is the structure of m/z 132 ($C_9H_{10}N$) in the EI spectrum of **1**; its CAD spectrum matches that of the reference ion $PhNH^+{=}CHCH{=}CH_2$, a homologue of (a). (A more straight-forward way to identify the piperidine ring of **1** would be to show that the CAD spectrum of its m/z 110 ions matched that of (f) Scheme I.) Consistent with the STIRS (*4, 5*) prediction of β-phenylethylamine, the $PhCH_2-$ group should be located on the α-C of the cyclic N (Figure 2). A logical place for the C_2H_5CO- group is on the other nitrogen, as propionamide ions commonly lose $CH_3CH{=}C{=}O$ (*23*). Thus the evidence leads directly to the China White structure. Although the data are much less consistent with other possible structures, this opinion may be biased by our prior knowledge of the correct structure.

Mechanisms of Piperidine Ion Decompositions. The uniqueness of the assignment of structure **1** is reinforced by

Table II. Even-Electron Ions from Rearrangements

				ion product, m/z							
compd	R^1	R^2	R^3	132	146	160	188	202	216	203	259
4[a]	H	H	H	25[b,c]	100[d,e]	5[f]	4[g,h]	15[i,j]	1[f]	2	3
1	CH_3	H	H	16[b,c]	32[d,e]	1[f]	<1[g,h]	8[i,j]	2[f]	17	100
2	H	CH_3	H	37[c]	13[b]	33[d]	<1[h]	48[g,j]	12[i]	25	100
3	H	H	CH_3	39[c]	8[b]	100[d,e]	<1[h]	3[g]	28[i,j]	43	77

[a] m/z 189, 43%; 245, 93%. [b] Can be formed by mechanism A as $PhN^+H{=}CHCR^3{=}CHR^2$. [c] By A' as $PhN^+H{=}CHCH{=}CH_2$. [d] By B as $PhN^+H{=}C(CH_3)CR^3{=}CHR^2$. [e] By B' as $PhN^+H{=}C(CH_2R^3)CH{=}CH_2$. [f] Formed by none of these mechanisms. [g] By A as $C_2H_5CON^+(Ph){=}CHCR^3{=}CHR^2$. [h] By A' as $C_2H_5CON^+(Ph){=}CHCH{=}CH_2$. [i] By B as $C_2H_5CON^+(Ph)C(CH_3)CR^3{=}CHR^2$. [j] By B' as $C_2H_5CON^+(Ph){=}C(CH_2R^3)CH{=}CH_2$.

the mechanistic rationalization (Scheme I) of major peaks in the EI mass spectra of compounds 1–4 and 8 (Table II). The CAD spectra indicate that a major portion of these secondary ions is formed through the $(M - \cdot CH_2Ph)^+$ peak.

Besides the methyl ketene elimination discussed above, for these EE ion decompositions two pathways (A and B) are proposed which are applied to both cyclic EE ions, $(M - \cdot CH_2Ph)^+$ and $(M - \cdot CH_2Ph - C_3H_4O)^+$. Pathway A (illustrated in Scheme I only for m/z 203) could be triggered by hydrogen rearrangement to the charge site (*23*), after which olefin elimination would give the resonance-stabilized immonium ion. For pathway B inductive cleavage at the charged ring nitrogen followed by two H rearrangements would yield the homologous immonium ion incorporating an additional ring carbon as a methyl group. In general (Table II), pathway B is favored over A, in particular for those ions which still contain the propionyl group. This would be expected on enthalpic grounds; both the ion and neutral products of B have an extra methyl group to provide stabilization, while the extra C_2H_4 formed by path A has a slightly positive heat of formation. For the 2-methyl compound (**2**), however, the CAD spectrum of the m/z 146 formed by EI matches that of $PhN^+H{=}CHCH{=}CHCH_3$ (b), so that these ions arise mainly by pathway A, not B'. The initial C–N bond cleavage in path A could be enhanced by the presence of the 2-methyl to stabilize the charge transferred to the 2-carbon.

The analogous compounds **5–8** could conceivably decompose by similar mechanisms following ionization, but the CAD spectra of their $C_{10}H_{12}N^+$ ions (Table I) are substantially different than that of isomer (a) (path B). Those ions originating from **5** appear to be largely $PhCH_2N^+H{=}CHCH{=}CH_2$ (e), and so contain the terminal $PhCH_2N$ group of this compound; this isomer is formed to a lesser extent in the analogous compound **7**. This interference should not be a problem with seven-membered ring compounds **6** and **8**, but the CAD spectra of their m/z 146 ions indicate that these contain isomers in addition to (a–e). Although the large m/z 77 peaks in these CAD spectra indicate that the nitrogen is adjacent to the phenyl, we have not been able to prepare a reference ion whose CAD spectrum alone, or combined with (a–e), is consistent with these. If **6** and **8** had been unknowns, however, these m/z 146 CAD spectra would at least have indicated the absence of the piperidinyl substructure.

CONCLUSIONS

The utility of mass spectrometry for molecular structure determination of larger molecules is enhanced by substructure identification using CAD spectra of fragment ions. Expansion of the data base of CAD reference spectra (*15*) should make such substructural information much more readily usable for submicrogram samples for which methods such as nuclear magnetic resonance do not have sufficient sensitivity.

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